

Growth of Titania Nanowires by Thermal Oxidation

DISSERTATION

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By

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Abstract

Due to the unique properties of nanostructured metal-oxides, derived from their extremely small size scale in at least one dimension, several techniques have been developed for their production. However many of these techniques involve the use of chemical additives which could impact device performance, require costly processing equipment and highly trained personnel, or are difficult to scale up for mass production. In this dissertation a novel technique for the production of nanostructured titanium dioxide (TiO_2) by thermal oxidation of titanium and several of its alloys is presented. Two separate oxidation processes are described for the production of nanowires on titanium alloys and on commercially pure titanium (CPTi). The first involves oxidation in an oxygen deficient environment to promote the growth of 1-D nanowires. It was found that the oxidation temperature as well as the oxygen concentration play an important role in nanowire formation. A brief discussion is offered to explain the transition from planar oxide growth to highly anisotropic 1-D nanowires on the titanium alloy samples. Oxidation in an oxygen deficient environment was less successful at producing nanowires on CPTi. Thus, an alternative method of oxidation in a humid environment is presented as a means of increasing nanowire yield on CPTi substrates. Several applications for the nanostructures produced by these methods are presented and future research directions are suggested. For example oxidation of Ti-6%Al-4%V (Ti64) alloy, widely used for biomedical applications, to produce nanostructures has been

investigated as a means of improving cell adhesion and proliferation on medical implants. The nanowires grown on CPTi have been used as a precursor for hydrothermal conversion to barium titanate, a perovskite structure exhibiting ferroelectric behavior at room temperature. The unique morphology of the nanostructured TiO₂ precursor results in the formation of dendritic barium titanate, a unique structure seldom reported for this material. These and other exciting applications have been explored demonstrating the potential for industrial application of the low-cost methods to produce nanowires. Both oxidation processes for the production of TiO₂ nanowires on titanium substrates are low cost and are easily scalable for mass production of TiO₂ nanowires giving them a distinct advantage over other nanowire production methods.

Dedication

This document is dedicated to my wife Nancy and my two sons James and Paul for without their love and support I may never have undertaken this adventure.

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Chapter 1: Introduction

1.1 Introduction to Nanostructures

Nanostructured materials such as nanobelts [1-4], nanotubes [5-12], and nanowires [13-17] have garnered much attention due to the promise of enhanced or unique properties. These unique properties can be a result of the nanostructure's dimensionality [9, 18, 19], enhanced surface area [11, 20-22], quantum confinement [23, 24], or electronic properties [25-27] which can differ greatly from those of their bulk counterparts. This has driven a great deal of research into the fabrication, characterization, and application of nanostructured materials.

1.2 Applications of Nanostructured TiO₂

Nanostructured titanium dioxide (TiO₂) has been of particular interest in applications such as chemical sensors [28-30], photo-catalysis [31-33], and dye-sensitized solar cells [10] and is known for its biocompatibility. Titanium and titanium alloys have been widely used for orthopedic and dental applications because of their good biocompatibility, excellent corrosion resistance, and mechanical strength.[34] It has been reported that nanostructures of TiO₂ with grain/particle size less than ~100 nm drastically improves bioactivity of implants and enhances osteoblast adhesion.[35, 36] Thus, it is desirable to have a low-cost method for producing nanostructured TiO₂ directly on

titanium metal. Several techniques have been employed to produce nanostructured TiO₂ including hydrothermal [37, 38], anodization [35], etching [39], and deposition from a vapor phase [40]. However many of these techniques involve the use of chemical additives which could impact device performance, require costly processing equipment and highly trained personnel, or are difficult to scale up for mass production. In this document a novel technique for the production of nanostructured titanium dioxide (TiO₂) by thermal oxidation of titanium and several of its alloys is presented. The presented oxidation processes is low cost and easily scalable for mass production of TiO₂ nanowires giving it a distinct advantage over other nanowire production methods.

1.3 Introduction to Nanoscale Nomenclature

The term “nanostructure” is used ubiquitously throughout this document and simply refers to structures having at least one dimension in the 1 to 999 x 10⁻⁹ m regime. Often, a structure having at least one dimension in the nano regime will have “nano” as part of its name with the rest of the name being a description of what the structure looks like. For example, a nanoribbon would be a wide flat structure with at least its thin dimension less than 1 μm. A nanowire is a wire shaped object whose radial dimension is in the nanometer regime. Nanowire is used extensively in this document and therefore will be abbreviated NW. The plural form, nanowires, will be abbreviated NWs.

1.4 Organization of Dissertation

This dissertation is organized with the assumption that the reader has no prior knowledge of nanostructured growth techniques or titanium, its alloys, and oxidation behavior. Two background sections are presented, Chapter 1 and Chapter 2, the first of which is

designed to bring the reader up to speed on current vapor phase growth techniques used to produce NWs and the mechanisms, where known, that have been used to explain the one dimensional growth. Chapter 2 introduces titanium, its properties, the effect of alloying elements, and its oxidation behavior.

The background sections are followed by an introduction and discussion of the growth of NWs on titanium alloy samples by oxidation in an oxygen deficient environment. This is followed by a discussion of a proposed mechanism to explain the highly anisotropic growth of the oxide on alloy substrates. The oxidation of titanium alloys in an oxygen deficient environment produces well defined nanostructures but is less effective at producing NW growth on commercially pure titanium samples. As such, an alternative method of oxidation in a humid environment is presented which results in improved NW growth on commercially pure titanium.

Chapter 7 explores several applications for the nanostructures which are currently being explored. The dissertation ends with a discussion of several conclusions which can be made for both the dry and wet oxidation processes and provides directions for future work for both of these systems.

Chapter 2: Nanowire Vapor Phase Growth Processes: A Literature Review

2.1 Nanowire Growth Methods: A Literature Review

A great many fabrication techniques have been developed to produce one dimensional (1-D) nanostructures. These techniques can be divided into two main approaches depending on where the production of the nanostructure starts: top-down and bottom up. The top-down approach is capable of producing both nanorods and NWs using the same techniques commonly employed in the production of microelectronic devices.[41-43] Martinez *et. al.* successfully fabricated a Si NW based transistor using atomic force microscopy (AFM) and selective chemical etching. The AFM was used to create nanoscale masks on Si substrates. The substrates were then etched to produce Si NWs; source and drain contacts were subsequently deposited using electron beam lithography.[43] **Figure 2.1** shows the transistor at multiple levels of the production process. Some advantages of the top-down approach include the accurate control of diameter and length of the nanostructures, techniques involved are well established and understood, and complex nanostructured patterns can be developed and used. However, many of these techniques require highly trained personnel and very expensive equipment. Additionally, materials for nanostructure production are limited to those used in the microfabrication industry. The size scale is also limited to the resolution of the

lithography technique being employed. Due to these limitations and the complex procedures typically evolved in these processes, wide spread implementation of lithography as a means of producing 1-D structures has been slow. Instead, much of the focus has been on the production of 1-D nanostructured materials by the bottom-up approach. The following section briefly describes several processes utilizing the bottom-up approach.

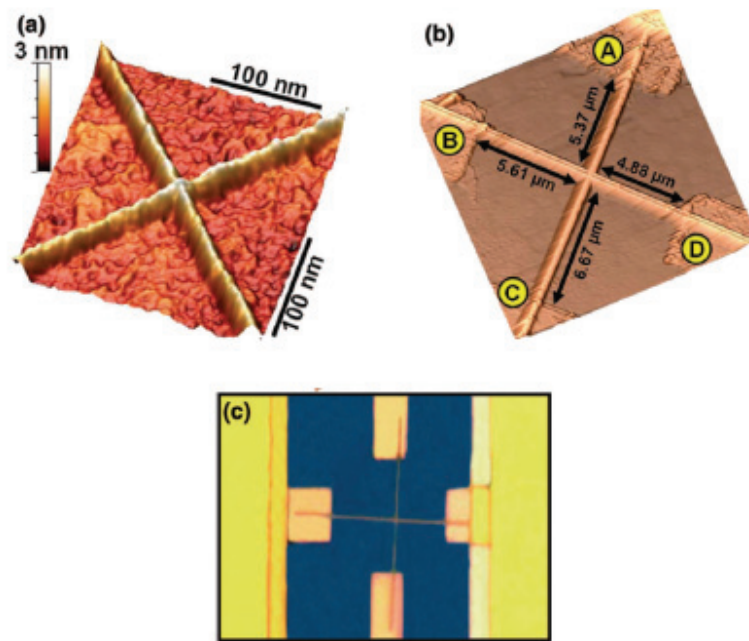


Figure 2.1: Amplitude modulated image of (a) SiO₂ NW mask produced by local oxidation via AFM, (b) device after chemical etching and removal of the SiO₂ NW mask but before source and drain deposition, and optical image of (c) the final NW transistor.[43]

2.2 NW Growth Processes

Growth processes by the bottom-up approach can involve a gas phase reaction of a vapor species and a substrate or can occur in solution. The desired end application often dictates

which process is best suited for the production of nanostructures. Solution grown nanostructures, usually achieved by precipitation reactions, are capable of yielding highly uniform products which are well dispersed. However, these types of processes often require very precise control of the chemical properties of the solution (e.g. pH, viscosity, etc.) and can contain contaminate species in the precipitate precursors, which require removal once the reaction has completed. Additionally, post treatments including cleaning, compaction, and sintering are often required for integration or fabrication into a device thus adding both cost and complexity to the processes. Nanostructures produced in solution are a topic unto themselves and are outside the scope of this document. Instead, nanostructures produced by means of gas phase reactions will be discussed.

Vapor phase assisted growth is one of the most common means for producing nanostructures, often NWs, on a desired substrate. The vapor phase constituents can be a metal, as is the case with vapor-solid (VS) and vapor-liquid-solid (VLS), or it can be an oxygen-bearing gas as with growth by oxidation. Several techniques have been used to produce the vapor phase constituents needed for growth by both VS and VLS including laser ablation [8], thermal evaporation [44], carbothermal evaporation [45, 46], and metal organic precursors in the gas phase [13, 47, 48]. This approach has several advantages over solution methods. First and foremost, the nanostructures can often be grown directly onto a desired substrate, allowing for easy integration into an existing device or product during the production process. Additionally, a tight control over chemical reactants, compared to those required in solution treatments, is not typically

necessary for these processes, thus allowing for both a wider margin of error in processing and a reduction in manufacturing costs.

2.3 Vapor-Liquid-Solid (VLS) Method

Of the vapor phase growth methods, the VLS method is the most widely used and best understood. In general, a vaporized source material is introduced into a reaction chamber and flown by a carrier gas downstream. As this vaporized constituent deposits on a substrate surface there must be a means of confining the deposition to limited surface locations for the process to produce nanostructures. Otherwise, only a uniform film would develop. One of the most successful ways to provide this confinement is through the use of a liquid metal catalyst. This is the basis of the VLS mechanism. A catalyst in the liquid phase, typically a metal, provides preferential deposition sites for the vaporized source material and gives the chemical adsorption confinement required for one dimensional growth.[49]

With VLS, liquid droplets are formed by eutectic reactions between a source material and the catalyst. The liquid droplets have a finite solubility of the vaporized source material thus providing favorable sites for the adsorption on the surface and subsequent absorption into the catalyst droplet. Once this solubility limit is exceeded, the source material adsorbed on the droplet diffuses to the liquid-solid interface of the substrate creating nucleation sites for the 1-D growth of the nanostructures.[49] The confinement is provided by the enhanced adsorption and diffusion of the vapor species on and into liquid catalyst. This allows for a higher reaction rate of the nanostructure forming constituents at the liquid droplet than that of the surrounding area, resulting in the confinement of

growth to one dimension. Upon cooling, the liquid catalyst solidifies, producing a cap on the tip of the nanostructure. The presence of this cap is a so called smoking gun of the VLS mechanism. There have been a variety of nanomaterials including Si [49], SiO₂ [50], InAs [47], TiO₂ [51, 52], ZnO [53], SnO₂ [45, 54], and GaN [55] with various morphologies produced by this technique.

An example of one such structure, as presented by Wagner and Ellis who first reported the VLS mechanism in 1964, is Si nanowhiskers grown using Au as the catalyst. For this experiment, a small particle of Au was placed on a (111) silicon substrate. It was subsequently heated to 950°C where a liquid droplet of Si-Au formed (**Fig. 2 a**). A gas mixture of H₂ and SiCl₄ was flown over the sample. The Si-Au liquid droplet allows for preferential adsorption of Si in the vapor phase. Once the alloy droplet reaches the saturation limit for Si, the Si solidifies at the droplet-substrate interface. As this process progresses, the Si-Au droplet is pushed up by the growing Si single crystal nanowhisker (**Fig. 2 b**). This process continues until either no more Si remains in the vapor phase.[49]

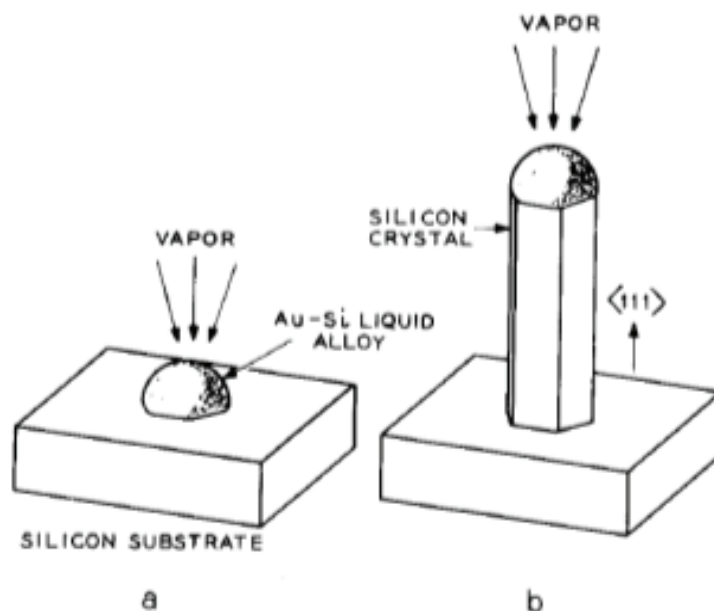


Figure 2.2: Schematic representation of the growth of NWs by the VLS mechanism. a) Initial droplet formation as catalyst site. b) Growing NWs with metallic alloy at the tip.[49]

Similarly, TiO₂ NWs were grown in a comparable process again using Au as the liquid catalyst.[32] In this study, a Ti thin film was deposited on a substrate by DC magnetron sputtering, a subsequent Au layer was added, and the sample was placed in a horizontal furnace. Ti powder was then placed upstream and heated to 1050°C while the substrate was maintained at 750°C. The Au formed liquid droplets at this temperature providing the catalytic sites necessary for 1-D growth. High purity Ar (99.999%) was flown through the furnace carrying the vaporized Ti downstream for condensation on the substrate. By this process Wu *et. al.* were able to produce high aspect ratio TiO₂ NWs with lengths up to 3 μm and diameters in the range of 60-90 nm.[32]

Although Au is the most widely used metal catalyst used in the VLS growth method it is not the only catalyst used. Chen *et. al.* investigated many catalyst including metal powders of In, Co, Ni, Fe, Ni/Co, and Fe/Co as well as metal complexes of ferrocene, iron phthalocyanine, cobalt phthalocyanine and nickel phthalocyanine when attempting to reproducibly grow high-purity, high-quality crystalline GaN NWs for reliable testing of their optoelectronic properties.[56] The catalysts were suspended in either toluene or water by sonication and then dispersed on a silicon (100) substrate and dried in a tube furnace under flowing nitrogen. Upstream, gallium was placed on an alumina substrate and heated to 910°C and ammonia was flown as the carrier gas for a reaction time of 12 hours. It was found that all catalysts under investigation produced NWs with high aspect ratios; however, depending on whether the catalyst was a metal powder or a metal complex, the range of NW diameters varied significantly. NWs produced using a metal powder catalyst had typical average diameters in the range of 20-100 nm while those produced using a metal complex as the catalyst had average diameter in the range of 10-50 nm with a minimum achievable diameter of 6 nm. It was theorized that the metal complexes decompose into gaseous species at higher temperatures forming very small catalytic clusters compared to the metal powders. These smaller clusters produced less catalytic area and thus, result in smaller average diameter GaN NWs.[56]

Baik *et. al.* also successfully grew NWs using a catalyst other than Au. Single crystal TiO₂ NWs were grown on Ti thin film, deposited via electron beam lithography, by atmospheric pressure chemical vapor deposition (APCVD) using Ni as the catalyst. TiO powder was placed in an alumina boat upstream from the thin film in a horizontal tube

furnace which was heated to 950°C and high purity Ar was flown as the carrier gas. This process resulted in NWs with mean diameters of 48 nm and lengths of 10-30 μm for a 2 hour process duration.[57] A small metallic droplet was easily visible at the tip of the NWs as seen in **Figure 2.3 a** (inset), a sure indicator of the VLS mechanism.

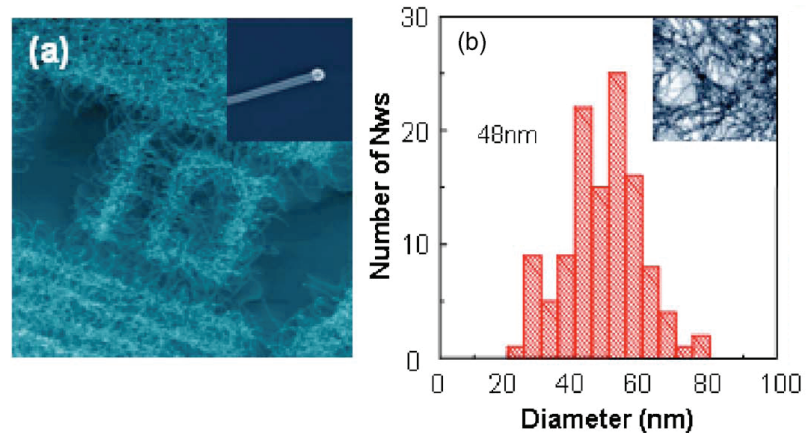


Figure 2.3: TiO₂ NWs grown by APCVD. (a) SEM micrograph showing a high density of NWs (inset) high magnification showing metallic cap formed by the VLS process. (b) NWs diameter distribution obtained by (inset) low magnification TEM analysis.[57]

These are but a few of the many examples of nanostructures grown by the VLS mechanism. While highly versatile and useful in its ability to be scaled up for mass production, this mechanism is not without its shortcomings, the most notable of these being the residual metal alloy cap left on the NWs post growth treatment. Depending on the desired application, this may cause an added step of complexity if the application requires a cap/impurity free nanostructure. One may be able to employ chemical methods to remove the metal cap but care must be taken to ensure that neither the nanostructure morphology nor the device itself is destroyed.

2.3.1 Vapor-Solid (VS) Mechanism

The presence of a metal catalyst is not required for the confinement of growth to one dimension from a condensed vapor phase. A vapor solid (VS) mechanism has been used to explain the growth of nanostructures where no external catalyst is used and the resulting nanostructures do not have a cap after the growth process has completed. The VS mechanism maintains that defects inherent to the substrate surface provide the growth confinement required to obtain 1-D nanostructures.

Originally, the VS mechanism was solely used to explain the growth of 1-D structures by chemical vapor deposition when no catalyst is used; however, due to a lack of fundamental understanding of the underlying growth mechanisms, it is now broadly used to explain almost all NW growth in which the main constituent of the resulting nanostructure exists in the vapor phase but no liquid phase catalyst is present. Of the mechanism described in this document, VS is the least understood but most widely used to explain 1-D growth. This lack of understanding stems from the unknown source of confinement to 1-D growth for these processes. Many theories have been developed to explain the 1-D growth without the use of a liquid catalyst including dislocation driven [58-62], stress/strain induced [63-65], nanocrystalline seeding [7, 66, 67], vapor phase condensation [68], and oxide-assisted growth [14, 69-71]. The following discussion highlights some of the specific distinctions between these different theories citing examples of nanostructures produced via the VS mechanism.

2.3.2 Dislocation Driven Nanowire Growth

The dislocation mechanism for the growth of 1-D nanowhisker was first postulated by Sears in 1955 based in part on Elshelby's theoretical work on screw dislocations in thin rods.[50] The mechanism was further refined by Sears and Brenner in 1956 as presented in this section. The basis for this growth mechanism is that any real surface has screw dislocations intersecting it which can act as deposition sinks under low super saturations.[62] If such a material is surrounded by its own super saturated vapor, deposition can and will occur at the dislocation steps. We can define the vapor pressure at the crystal surface as p and the equilibrium vapor pressure as p_o , then the super saturation ratio α is p/p_o and the super saturation σ can be defined as

$$\sigma = \alpha - 1 \quad (1)$$

If σ is very small, that is the vapor pressure at the crystal surface is only slightly larger than the equilibrium vapor pressure, growth of the crystal can only occur by the Frank mechanism.[72] If screw dislocations intersecting the crystal surface are spaced sufficiently far apart, that is they are sufficiently separated from one another, growth in the shape of a cone, as seen in **Figure 2.4 a**, can occur. In this schematic the concentration gradient of the vapor species is shown as a series of dots. As this cone continues to grow it begins to rob the base of the structure of its share of diffusing atoms. This is a self-perpetuating process and due to the faster diffusion rate at the top of the cone, the distance between the steps is smaller and a tapered hill begins to form (**Fig. 2.4 b**). Eventually the cone will have a columnar summit as shown in **Figure 2.4 c** which will

continue to grow at a constant rate dependent on the super saturation as well as on the gaseous and surface diffusions.[62]

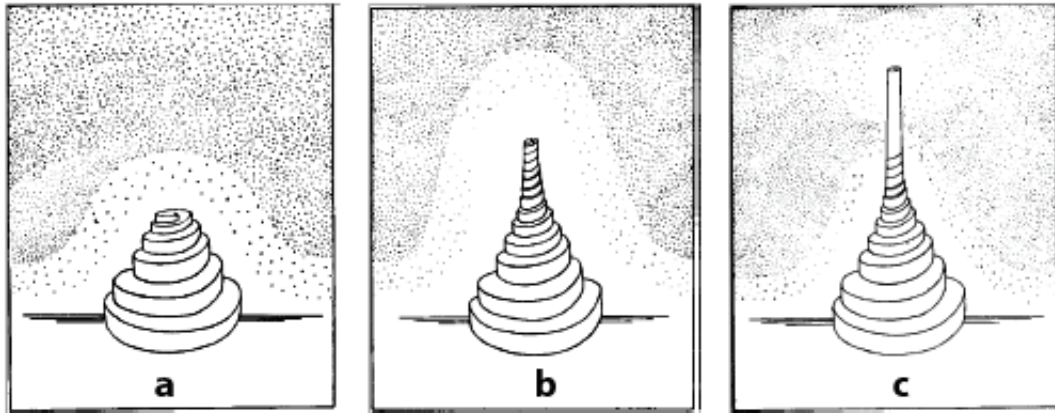


Figure 2.4: Schematic representation of the dislocation driven growth mechanism presented by Sears and Brenner. a) Atoms from the vapor phase preferentially deposit on steps formed by screw dislocations intersecting the surface of a crystal creating a cone. b) Diffusion at the top of the cone is faster than at the base leading to smaller step sizes at the top. c) Eventually the cone will grow at a constant rate.[62]

Using this mechanism, Sears successfully grew nanowhiskers of zinc, silver, cadmium, cadmium sulfide, lithium fluoride, and alumina.[50, 73, 74] Brenner also reported growth of nanowhiskers of iron, gold, cobalt, nickel and platinum by this mechanism.[62]

Although this mechanism has been widely accepted, until recently there had been no reports of direct observations of the screw dislocation theorized by Eshelby running through the length of NWs even though extensive characterization studies had been performed. Recently, Wu et. al. reported chiral branched PbSe NWs grown by a combined VS (dislocation driven) and VLS mechanism.[61] Their NWs consist of a core-branch structure where the core is grown by the dislocation driven mechanism.

Using TEM analysis they were able to identify a screw dislocation running down the center of the core. The branches, coming out perpendicular from the core, were grown by the VLS mechanism using lead as the catalyst and did not have dislocations running axially through their cores.[75]

2.3.3 Stress Induced Nanowire Growth

Another interpretation of the VS mechanism attributes the growth and confinement of nanostructures to 1-D to chemically active sites produced by cracks formed in a thin film due to strain relaxation. NW growth on a bulk material by gas phase reaction typically involves an initial deposition of a planar film prior to the transition to one dimensional growth. The planar film and bulk substrate often have differences in their lattice parameters and/or crystal structures resulting in a lattice mismatch between the two. A stress relationship develops due to this mismatch. Alternately, a stress relationship can be developed during the NW growth process itself by differences in the thermal expansion coefficients of the planar film and the bulk substrate. The stress induced NW growth theory attributes this relationship to the formation of nucleation sites for subsequent preferential deposition of the vapor species. Prokes and Arnold successfully grew Si nanowhiskers by heating Si substrates in an Ar/H₂ environment. They found that the presence of a SiO₂ layer was critical to the formation of the wires. The thermal expansion coefficient of the SiO₂ layer is roughly an order of magnitude smaller than that of the Si substrate.[64] Upon heating, this difference caused the oxide layer to come under a tensile stress while the bulk Si was under compressive stress, resulting in the formation of cracks in the SiO₂. These cracks form to relieve the area surrounding it of its stress

leaving a stress-free region compared to the uncracked region resulting in a stress gradient. This stress gradient led to the migration of Si atoms from the compressed region to the stress free cracks creating an accumulation of Si in this area and the nucleation of nanowhiskers out of the cracks.[64] NWs formed only in the cracked regions as shown in **Figure 2.5**. It was also found that hydrogen played a crucial role in the growth of the nanowhiskers; without it no wires grew. It was deduced that hydrogen, known to increasingly stick on a Si (111) surface with increasing temperature and to increase the surface diffusion of Si, enhanced the diffusion kinetics such that 1-D growth is maintained. [76, 77]

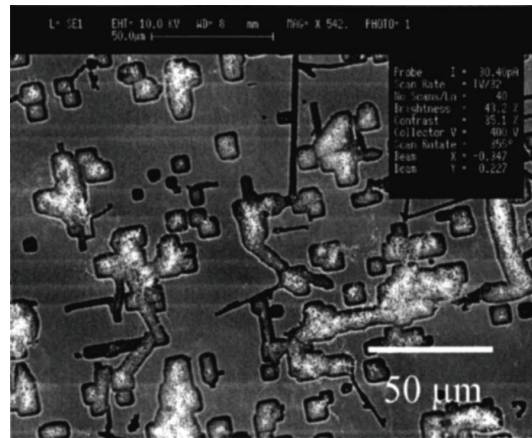


Figure 2.5: SEM micrograph of a Si wafer annealed in Ar/H₂ to produce NWs (white areas). NWs grew only in cracks formed by stress due to difference in the thermal expansion coefficients of the Si substrate and SiO₂ surface layer.[64]

2.3.4 Nanocrystalline Seeding

Catalyst-free growth of both single crystal Si and Ge NWs have recently been reported.[66] The resulting NW growth was attributed to the VS mechanism; however,

the interpretation of the mechanism differs from those outlined in the previous sections. The confinement to one dimension is not attributed to screw dislocations intersecting the crystal surface nor to the accumulation of atoms due to a stress gradient. Instead, the confinement to 1-D growth is attributed to the formation of reactive nanocrystalline seeds formed by the decomposition of an adsorbed precursor on a reactive oxide layer.[66] To create the reactive oxide layer, ultra pure water was used to etch hydrogen terminated Si wafers producing a silicon rich oxide layer. Seed formation was initiated at an initial processing temperature of 520°C and then reduced to 490°C for the remainder of the growth process. The temperature was decreased to limit nonspecific decomposition of SiH₄ on the NW surface.[66]

L.C. Chen *et al.* utilized a non VLS process for growing high-purity silicon carbon nitride (SiC_xN_y) nanorods.[15] They also attribute their growth confinement to one dimension to the formation of nanocrystalline seeds. The first of two steps involved was the deposition of a SiC_xN_y film seed layer by electron cyclotron resonance (ECR) plasma enhanced chemical vapor deposition (PECVD) on top of a Si wafer heated in the temperature range of 200°C - 900°C. The sample was then transferred to a microwave reactor for a second PECVD step. SiH₄ diluted in N₂ was used as the source gas for the resulting nanorods. It was found that of the processing variables investigated, substrate temperature during the initial seed layer deposition had the greatest influence on the resulting morphology.[15] At a high enough temperature the seed layer formed nanocrystallites which served as preferential nucleation sites for subsequent nanorod growth. If the substrate temperature was below 240°C, only an amorphous layer of SiC_xN_y formed. The coverage of

nanocrystallites formed at the surface of the buffer layer dictated the resulting density of the nanorods. Without the 1-D confinement provided by the nanocrystallites, no nanorod growth occurred and only a thick amorphous layer formed. It is believed that the nanocrystallites form as a direct result of stresses induced in the seed layer during ECR-PECVD. When the processing temperature is high enough, the amorphous film elevates some of the stress by forming the nanocrystallites.[15]

2.3.5 Growth in Gas Phase and Subsequent Condensation

Another example of vapor phase growth of nanostructures without the use of a liquid catalyst and thus attributed to the VS mechanism is the work of Yuvaraj *et al.* who successfully grew ZnO nanoneedles on glass slides at room temperature by activated reactive evaporation (ARE).[17] This process has a significant advantage over most other vapor phase growth methods in that it does not require the very high processing temperatures typical of vapor phase growth processes. Zn was evaporated by resistive heating and ionized oxygen was used as the transport gas. It was found that the nanoneedles form in the gas phase and are continuously transported in the gas and subsequently deposit on glass substrates as nanostructured films.[17] The growth of the nanoneedles is attributed completely to the VS mechanism however the only similarity to the previously discussed mechanisms is the growth precursor, Zn, exists in the vapor phase. The other descriptions of the VS mechanism all involve interactions with the substrate as the means for confinement to 1-D growth. This method only involves the condensation of the nanoneedles on the substrate after forming in the gas phase. In fact, an extensive investigation into the role of substrate surface roughness in the nanoneedle

growth process was conducted. The results showed that surface roughness played a negligible role in the formation of nanoneedles.[17]

The previous four sections have been devoted to describing methods and mechanisms often used to explain the growth of nanostructures from chemical vapor deposition methods. Each of the previous examples attributes, at least in part[61, 75], the growth of their respective nanostructures to the VS mechanism. It is clear however, that the mechanism for growth and confinement to 1-D is not the same in all of these cases. For example, some attribute the growth defects in the substrate interface to providing chemically active sites which allow for preferential deposition and subsequent decomposition of the gaseous precursor while others maintain that nanostructured growth occurs in the gas phase and deposits by condensation alone on to a substrate. These two mechanisms, while completely plausible, are in stark contrast to one another and as such should not fall under the same mechanism umbrella. One can argue that the dislocation driven and nanocrystalline seeded growth can both be caused by stresses in the substrate material providing preferential deposition sites for incident precursor material, thus relating the first three mechanisms discussed to one another, but this does not account for the appearance of dislocations in the core of some structures and not in others. There is another type of nanostructured growth which is often attributed to the VS mechanism: growth by oxidation. Unlike the previously discussed examples, growth by oxidation is not a chemical vapor deposition process but rather an oxidation process and as such should be considered a category unto itself. The following sections are devoted to the

discussion of nanostructured growth by oxidation: its advantages, disadvantages, and the current understanding of the growth mechanisms involved.

2.4 Thermal Oxidation

Most of the growth methods discussed to this point, often lumped under the umbrella of the VS mechanism, involve nanostructured growth by chemical vapor deposition and as such are still in keeping with the original intent of the of VS mechanism, even though the interpretation of the mechanism may be different. However, recent reports have attributed 1-D growth of oxide nanostructures in which the main chemical species in the vapor phase is oxygen to the VS mechanism.[78] While it is true that a vapor species, oxygen, is depositing and reacting with a substrate to form 1-D structures, oxygen is the only vaporized source material for the 1-D structures. This small distinction separates this growth process from the majority of processes which are commonly attributed to the VS mechanism.

Semiconducting oxides have been of great interest to the nanomaterials community due to their photoelectronic [3, 21, 45, 79-82], electrical transport [25, 27, 83], and chemical sensing [20, 29, 30, 84-86] properties. SnO_2 -(α - Fe_2O_3)-based nanoparticles, for example, have been found to have an extremely high sensitivity to small concentrations of ethanol gas.[86] Additionally, ZnO NWs have been shown to work as optical resonance cavities effectively producing room temperature, short-wavelength nanolasers.[53] The VLS method can be employed to produce oxide nanostructures but this method results in the presence of the catalyst cap on the nanostructures which can result in the degradation of the properties which make semiconducting oxides so interesting. The VS mechanism is

also attractive for the growth of 1-D semiconducting oxides but the high temperatures required to produce sufficient vapor species for subsequent deposition and growth can be both costly and damaging if the oxide structures are to be grown on an existing device. For example, the melting points of titanium and TiO_2 are 1660°C and 1840°C , respectively, so the annealing temperatures required to produce the vapor pressure necessary for growth by chemical vapor deposition would be quite high requiring a very high temperature furnace. If the nanostructure is to be grown directly on a device, every component of the device would need to be able to withstand these high temperatures. To overcome the limitations of the VLS and VS methods of nanostructured growth for semiconducting oxides, growth by means of oxidation has been used.[14, 16, 71, 87-91] It is important to note that this method is not well understood. The confinement of growth to one dimension is still unknown although several theories for individual systems have been developed and will be discussed in the following section. What is known is that there is insufficient vapor pressure of the metal species for growth by chemical vapor deposition and no external catalyst is introduced nor is there evidence after growth of a cap on the nanostructures; thus allowing for elimination of both the VS and VLS mechanism as the means for 1-D growth.

2.4.1 The Oxidation Process

To develop an understanding of the growth of nanostructures by oxidation it is important to understand the oxidation process. One of the most studied and best understood systems for oxidation is the Si-SiO₂ system. It has been widely used in the semiconductor and microelectronics industries for many years, so much is known about the specific

interactions and processes governing the growth of SiO₂ from a Si substrate. We will use this model to explain the simple oxidation of a substrate before discussing some of the interpretations of the mechanisms allowing for growth confinement to 1-D of some oxide nanostructures.

To begin, some oxide is almost always present on the surface of a material due to atmospheric oxidation, typically 10-20 Å thick.[92] For oxidation to occur, oxygen must reach the Si interface. As the oxide grows it becomes thicker and the oxygen must pass through more and more oxide. As a result, the growth rate of the oxide layer reduces over time. For the sake of this discussion we will make the approximation that everywhere in the oxide the oxygen flux is constant. The oxygen flux then becomes a function of the oxide layer thickness and the concentration of oxygen at both the surface of the oxide and the oxide-substrate interface. This is shown schematically in **Figure 2.6 a**. At the SiO₂-Si interface the oxidation rate is proportional to the concentration of oxygen such that the flux is directly proportional to this concentration. The rate of change of the oxide layer thickness can be related to the oxidation flux divided by the total number of the oxidizing species molecules in a unit volume of the oxide. For short oxidation times, the growth rate of the oxide is limited by the reaction at the substrate interface. For longer times the growth rate of the oxide layer is diffusion limited.[92]

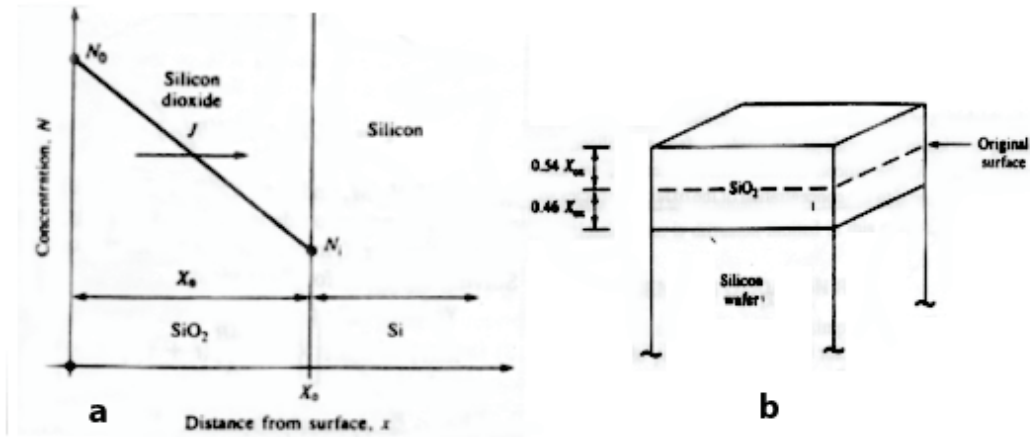


Figure 2.6: Schematic representations of a) the concentration gradient of oxygen through an SiO_2 layer where X_0 is the thickness of the SiO_2 layer and N_0 and N_1 are the concentration of oxygen at the SiO_2 surface and SiO_2 - Si interface respectively and b) the relative percentages of the SiO_2 layer after oxidation above and below the original Si interface.[92]

There are several factors which can influence the oxidation rate of a material, including but not limited to crystal orientation, temperature, wet or dry environment, and impurities. For example, it is known that water vapor is much more soluble in silicon dioxide than is oxygen.[92] This leads to an increased growth rate of SiO_2 in a humid atmosphere. However this increase in growth rate results in a less dense oxide of poorer quality compared to SiO_2 grown in the absence of humidity.

In the preceding discussion, planer oxide films of regular thickness were grown by oxygen diffusing through an oxide layer to an oxide-substrate interface where the diffused oxygen reacts with the substrate-forming new oxide. However, it is also possible for substrate atoms to diffuse from the substrate to the oxide surface where they can react with adsorbed oxygen to form new oxide. In reality, for most systems, both processes occur but typically at differing rates. If we again look at the Si - SiO_2 system as a model,

an oxide grown by thermal oxidation of thickness X_o extends approximately half the distance below and half the distance above the original Si surface (**Fig. 2.6 b**). For this bidirectional growth to occur there must be outward diffusion of the Si atoms in addition to the inward diffusion of oxygen. If oxygen is diffusing in and Si is diffusing out, then there are 3 possible locations for oxide growth to occur: the Si-SiO₂ interface, the surface of the SiO₂ layer, or the diffusing Si and oxygen atoms could encounter one another and react inside the oxide layer. Which one of these is the dominant location for growth is dependent on the diffusion rates of the atoms involved. If oxygen is diffusing much faster than Si, the reaction will take place mostly on or near the Si-SiO₂ interface. If, on the other hand, Si diffuses much faster than oxygen through the oxide then the reaction will take place mostly on or very near the surface of the oxide layer. If the two rates are comparable to one another, then the reaction will take place inside the oxide layer. Now that we have established the basics for the growth of a planar oxide film by thermal oxidation we investigate some proposed mechanisms for the confinement of the oxide growth to one dimension to produce semiconducting oxide nanostructures.

2.4.2 Oxide Assisted Growth

A mechanism of oxide-assisted growth (OAG) has been proposed as a means of producing 1-D nanostructures by thermal oxidation. The process, as outlined by Zhang *et. al.*, proceeds as follows for SiO₂ NWs.[93] Silicon sub-oxide clusters, SiO_x clusters where $2 > x > 1$, are created on a SiO₂ substrate by laser ablation. These clusters are highly reactive and prefer to form Si-Si bonds with other clusters. Some of these form Si-Si bonds with the substrate effectively pinning them in place. These immobile clusters have

active Si atoms exposed to an ambient vapor with their dangling bonds facing outward from the cluster. These active bonds serve as nuclei capable of adsorbing other reactive clusters and promoting the growth of SiO₂ NWs. It is theorized that as the NWs grow, oxygen from the core is expelled to the outside of the NW forming a relatively inert SiO₂ outer layer and a Si-rich core. The claim is that the chemically inactive SiO₂ layer restricts further radial growth effectively confining further growth to only the axial direction.[93] The basis for this explanation, growth and confinement to 1-D, is almost purely theoretical. The only supporting evidence provided for this theory is that a constant source of SiO₂ is required for sustained growth and the resulting structures have a SiO₂ outer layer and a Si-rich core. If a pure Si substrate is used or if a SiO₂ seed layer is ablated and then Si vapor in the form of SiH₄ gas is introduced, no NW growth is seen.[93] Zhang *et. al.* have reported the growth of Ge, GaN, GaAs, GaP, ZnO and carbon NWs all by the OAG method. While this is an interesting theory for the growth of nanostructures by oxidation, further investigations into the specific surface reactions and interactions during the initial formation and continued growth of these structures are required.

Another mechanism for the growth of nanostructures by oxidation has been proposed by Peng *et. al.* who thermally oxidized Ti metal substrates at 850 °C in three different oxygen environments: high purity oxygen, a low oxygen concentration Ar mixture, and in acetone.[87] Both the low oxygen concentration mixture and the acetone heat treatments produced nanostructures but the high purity oxygen produced only a planar film. The samples oxidized in acetone produced well-aligned nanorod arrays while the low oxygen

concentration treated samples produced nanofibers several microns in length growing epitaxially from the surface of large TiO_2 grains. The difference in morphology between these three samples was attributed to the different growth rates of TiO_2 and to the difference in the dominating diffusion species, titanium and oxygen. The growth of the planar film in the high purity oxygen was explained by oxygen diffusion being predominant because of the high concentration of oxygen. It is theorized that TiO_2 is grown between the TiO_2 grains and the Ti metal surface resulting in the growth of very large TiO_2 grains.[87] The growth of the nanofibers from the low oxygen concentration mixture was attributed to the surface diffusion of Ti cations. All nanofibers formed by this process were seen growing from ledges of TiO_2 grains instead of from grain boundaries or smooth surfaces. This was explained by Ti cations diffusing to the grain ledges and reacting with the gaseous oxygen to grow the nanostructures. Although this explains why the growth occurs preferentially at the ledges, it does not explain how or why growth is confined to 1-D. The third process, growth in acetone, produced well-aligned arrays of nanorods. Here, the difference between nanofibers (grown in low oxygen environment) and nanorods is simply the difference in average diameter: nanorods ~500 nm and nanofibers ~200 nm. The availability of oxygen for the oxidation of Ti is much less in the acetone environment compared to either of the other two environments used.[87] Due to this, it was suggested that Ti diffusion was the predominant process in the growth of the oxide. A two step process was presented as the means of producing the nanorods. First, a very thin layer of TiO_2 formed through which Ti diffused by a network of grain boundaries in the oxide to react with the acetone on the

surface of the oxide. The confinement to 1-D is attributed to the preferential adsorption of acetone on specific TiO_2 faces resulting in preferential oxide growth on these faces. A more recent paper by the authors lists $\langle 001 \rangle$ as the preferred growth direction for the nanorods.[52] This paper also investigated the impact of temperature on the resulting nanostructures but added no further insight into the mechanisms involved.

The growth of cupric oxide (CuO) NWs makes for an interesting case study into the controversy and lack of understanding surrounding the oxidation growth mechanism and confinement of growth to 1-D. Several research groups have successfully grown CuO nanostructures by thermal oxidation but the interpretations of the underlying growth mechanisms differ. CuO NWs grown by oxidation have been observed on Cu TEM grids, Cu wires, and Cu foils after oxidation.[14, 16, 69, 78, 89, 91, 94-96] In 2002 Jiang *et. al.* reported one of the first mechanism studies on the growth of CuO NWs by thermal oxidation.[16] They had successfully grown CuO NWs on a variety of copper substrates by annealing the samples in air at temperatures between 400°C and 900°C . The length of the CuO NWs were dependent on the growth time and were found to grow at a rate $> 3 \mu\text{m/h}$. The average NW diameter was found to be a function of the processing temperature such that NWs grown at temperatures of 400°C , 500°C , and 600°C for 4 hours resulted in average diameters of 100, 75, and 30 nm, respectively. The NWs were bicrystalline where each side of the NW was a single crystal with a twin defect running down the center. Their findings indicated that a precursor was present in the form of Cu_2O prior to the formation of the final oxide (CuO). The governing reactions for CuO NW growth by oxidation as described by Jiang *et. al.* are as follows:



where equation 10 is the rate limiting step.[16] It is this slowed formation of CuO from the more volatile Cu₂O species that guarantees the vapor pressure of CuO is low, making it possible to maintain a uniform diameter as the growth of the NWs proceeds.

Xu *et. al.* also grew CuO NWs by oxidation; however, they used both compressed air and a wet environment produced by bubbling compressed air through water.[95] Both the oxidation temperature and annealing times were consistent with those used in the previously discussed process (400°C - 800°C for 4 hours). While the presence of Cu₂O during oxidation was discussed, no weight was given to its impact on the underlying growth mechanism. In fact, the factor attributed with the confinement of growth to one dimension was screw dislocations intersecting the surface of the foil; however, no evidence of any kind was given to support this claim. Instead, the high resolution TEM image provided by Jiang *et. al.* of a single NW containing a twin defect (**Fig. 2.7**) was referenced as evidence of the defect structure providing confinement to 1-D growth though no discussion was provided explaining how this defect was related to 1-D confinement.[95]

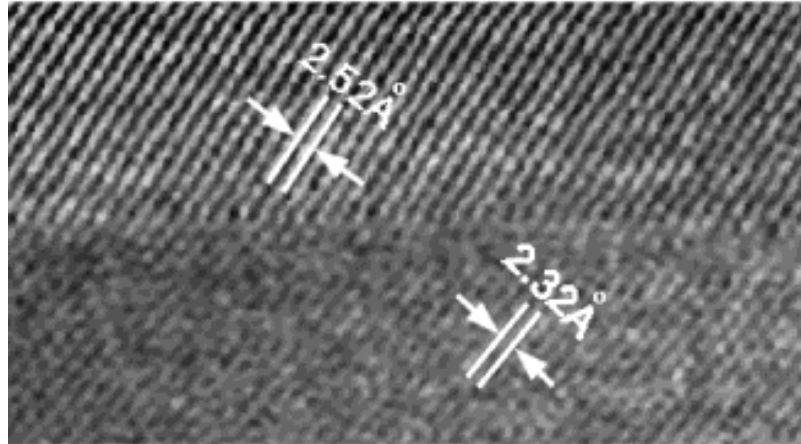


Figure 2.7: High resolution TEM image of a single CuO NW showing a well defined twin boundary separating to halves of the bicrystal.[16]

Others have directly refuted the claim that Cu_2O plays a critical role in the formation of CuO NWs. Kaur *et. al.* thermally oxidized copper foil in oxygen to produce NWs.[96] They ruled out the possibility of Cu_2O taking an active part in the formation of CuO NWs by oxidizing Cu_2O pellets in an attempt to grow CuO NWs. They were unable to produce CuO NWs on Cu_2O pellets under the same oxidation conditions as those used to grow the NWs on Cu foils. Due to this result, and to the fact that no Cu_2O was found at the cold end of their reaction chamber, Cu_2O was ruled out as playing a critical role in the growth of CuO NWs. If Cu_2O had been present in the chamber it would be an indication of the vaporization and subsequent deposition of Cu_2O possibly supporting the VS mechanism. Instead, Kaur *et. al.* attributed the growth of CuO NWs to a stress driven process. Stress formed by the fast growth of the oxide layer was thought to cause small crystallites of CuO to form which act as nucleation sites for preferential growth of the CuO NWs.[96]

Not all research groups were so quick to dismiss the role of Cu_2O in the formation of CuO NWs. Hansen *et al.*, who also studied the oxidation of Cu substrates as a means of growing NWs, paid careful attention to the resulting interface structure upon completion of the growth process. **Figure 2.8** shows an SEM image of the interface structure of Cu foil after oxidation at 500°C in air. The layered structure of Cu_2O , CuO film, and CuO NWs was confirmed by both X-ray diffraction (XRD) analysis and by electron dispersive spectroscopy (EDS).[89] The growth as outlined by Hansen *et al.* proceeds as follows: Cu_2O acts as a precursor for a slowly evolving CuO layer. The CuO layer provides a low vapor pressure of CuO localized at the growth sites thus promoting the growth of NWs.[89]

Through this case study it is easy to see how confused the issue of confinement of growth to one dimension can be. Just in the discussion of the oxidation Cu, several different growth mechanisms were given with no clear cut final solution to the problem. As a result more research is needed to definitively define the underlying growth mechanism which provides the confinement necessary to produce 1-D oxide nanostructures in a given system. Subsequent chapters in this document present two separate growth processes for producing TiO_2 NWs on commercially pure titanium (CPTi) and Ti alloys. The current understanding of the growth mechanism for NW growth on the Ti alloys is presented. NW growth on CPTi utilizes a different process than that of the alloy system and was developed after the Ti alloy NW growth process. As such, the mechanism is not as well developed. To aid in the understanding of both growth processes, it is helpful to have some background knowledge of Ti, its alloys, the role the alloying elements play in

the phase stability of Ti and the oxidation behavior of CPTi and its alloys in different environments. The following chapter is devoted to this purpose giving the reader a broad understanding of these topics.

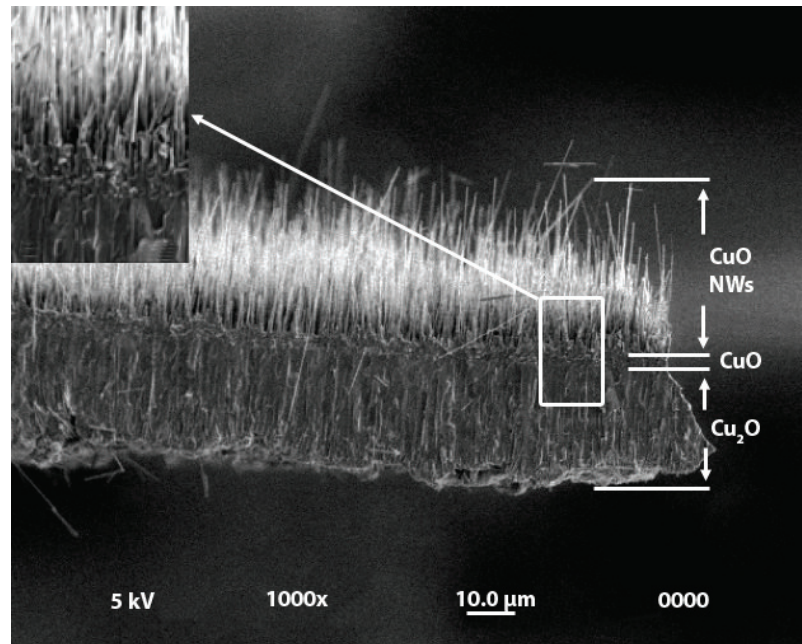


Figure 2.8: SEM micrograph showing the layered structure after the oxidation of Cu foil in air at 500°C. The layers consist of a Cu₂O sub layer followed by CuO file layer on top of which CuO NWs have grown.[89]

Chapter 3: Titanium: Structure, Alloys, and Oxidation

3.1 Introduction

Titanium (Ti) metal has been widely studied due to its combination of high strength, low density and excellent corrosion resistance.[97, 98] Traditionally, titanium use has been mainly within the aerospace industry where it has been used in airframes and engines due to its high strength to weight ratio and creep resistance at moderately high temperatures (up to approximately 550°C).[97, 99-101] More recently, Ti has been used in chemical processing equipment[102, 103], off-shore structures[104-106], biomedical implants and devices[34, 107], and consumer goods such as eye glasses and golf clubs[108]. What makes Ti such an attractive metal for these and other applications is the discussion of the following sections. A brief listing of the relevant Ti properties as well as an abbreviated discussion of several commercially relevant Ti alloys is presented. The chapter concludes with an introduction into the oxidation behavior of Ti and its alloys.

3.2 Properties of Titanium

At room temperature, titanium exists in the α -phase with a hexagonal close packed (HCP) crystal structure having lattice parameters of $a = 0.295$ nm and $c = 0.468$ nm giving a c/a ratio of 1.587. It has a room temperature density of only 5.507 Mg/m³. Ti undergoes an allotropic phase transformation at 1155 K (882°C) from HCP to body centered cubic

(BCC) with a lattice parameter of 0.332 nm at 1200 K. The high temperature BCC phase of titanium is referred to as the β -phase and has a density of approximately 5.35

Mg/m³.^[98]

Titanium's high strength to density ratio makes it an attractive material for many applications. **Table 3.1** lists several important characteristics of titanium along with those of other structurally relevant materials including Fe, Ni, and Al.^[97] Of the metals listed in **Table 3.1**, Ti has the highest strength to density ratio. However, its use is limited to only a relatively few applications compared to iron or aluminum due to its high cost. This high price is due in part to its high reactivity to oxygen.^[97] Thus, processing of titanium requires the use of either vacuum technologies or an inert atmosphere increasing the refining and manufacturing costs.^[109] Titanium's reactivity to oxygen is not entirely negative, when reacted at moderate temperatures (below 600°C) in air a stable oxide layer forms providing superior corrosion resistance to a variety of aggressive environments. Titanium's high melting point (1670°C) places it among the refractory metals making it suitable for high temperature applications.^[98] Additionally, its melting point is significantly higher than that of its main competitor in light weight structural materials, aluminum, giving it a significant advantage for applications in which temperatures exceed 150°C.^[97]

	Ti	Fe	Ni	Al
Melting Temperature (°C)	1670	1538	1455	660
Allotropic Transformation (°C)	β $\underline{882}$, α	γ $\underline{912}$, α	-	-
Crystal Structure	bcc \rightarrow hex	fcc \rightarrow bcc	fcc	fcc
Room Temperature E (GPa)	115	215	200	72
Yield Stress Level (MPa)	1000	1000	1000	500
Density (g/cm ³)	4.5	7.9	8.9	2.7
Comparative Corrosion Resistance	Very High	Low	Medium	High
Comparative Reactivity with Oxygen	Very High	Low	Low	High
Comparative Price of Metal	Very High	Low	High	Medium

Table 3.1: Some important characteristics of titanium and titanium based alloys as compared to other structural metallic materials based on Fe, Ni, and Al.[97]

The corrosion resistance of CPTi has been well document in a variety of environments including sea water[110], saline physiological solutions[111], and acidic environments[112]. Of the structural metals listed in **Table 3.1** titanium has the highest corrosion resistance with the only real competitor being aluminum. Both Ti and Al can attribute their excellent corrosion resistance to the native oxide layer on their surfaces. A detailed discussion of the oxidation of Ti is reserved for later sections however, many studies have investigated means to further improve the corrosion resistance of Ti and Ti alloys. For example, Mohsen et. al. successfully increased the corrosion resistance of CPTi in a phosphate saline buffer solution (PSB) by anodization.[113] PSB was chosen as the corrosion media to simulate implantation in the human body. A significant reduction in the polarization resistance (R_p) and the corrosion current (I_{corr}) for CPTi samples treated by anodization compared to untreated CPTi was reported. Additionally, they noted a further reduction in R_p and I_{corr} by sealing the anodically treated samples in

boiling water for 20 minutes.[113] No specific reasons were given for the improvement in corrosion resistance upon sealing in boiling water.

Titanium has a lower Young's modulus than nickel or iron but comparable yield stress as can be seen in **Table 3.1**. The reduced Young's modulus for titanium is drastically offset by its comparatively low density. **Figure 3.1** shows a plot of yield strength-to-density ratio as a function of temperature for titanium alloys compared to those of several other structurally relevant alloys.[98] The yield strength-to-density ratios for the titanium alloys are significantly higher than the other alloys. To improve the yield strength of titanium, alloying elements are often added to promote solid solution and precipitation hardening.[97] The additional elements are required because the α to β transformation in Ti happens rapidly and cannot be suppressed by rapid quenching.[98] The following section discusses some of the different alloying elements used for Ti alloys and their effects on the resulting Ti microstructure.

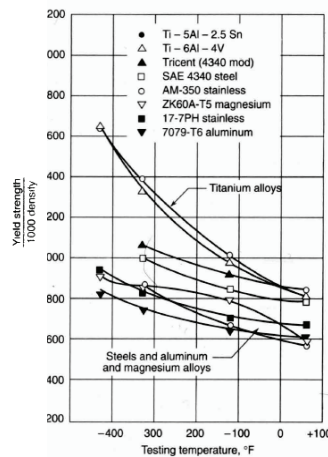


Figure 3.1: Yield strength to density ratio as a function of temperature for titanium alloys compared to other structurally relevant alloys.[98]

3.3 Titanium Alloys

The phase transition from α to β Ti has a strong dependence on both the amount and type of alloying element. Some alloying elements effectively raise the allotropic transformation temperature while others lower it. Elements that fall into the former category including oxygen, nitrogen, carbon and aluminum are known as α stabilizers as they increase the temperature to which the α phase is stable. In addition to altering the α - β transition temperature, all of these elements harden and solution strength α Ti.[98] Aluminum has considerable solubility in both the α and β phases and is a strengthening agent in both phases.

Elements which lower the α - β transition temperature are known as β stabilizers. These include chromium, iron, magnesium, molybdenum, and vanadium. In general, the β stabilizing elements have limited solubility in α phase. As a consequence, they strengthen the β phase by solution hardening but have little effect on the α phase. Often, a combination of α and β stabilizers are added to Ti alloys to strengthen both phases.

Figure 3.2 schematically illustrates the effects of various α and β phase stabilizing elements on titanium alloy phase diagrams.

Commercially available alloys can be divided into three categories: α or near α alloys, α + β alloys, and β alloys. A pseudo-binary phase diagram showing the distinction between these categories is shown in **Figure 3.3**. Alloys referred to as β alloys actually fall in the “Metastable β Alloy” category as true “Stable β Alloys” do not exist commercially.[97] Alloys which fall in the α alloy category include commercially pure grades of titanium.

The CPTi grades are distinguished by their impurity content. A higher grade CPTi contains lower levels of impurities and has lowered strength, hardness, and α - β transition

temperatures than lower grade CPTi.[98] These alloys contain only a very small fraction of retained β phase (2-5 volume %) after annealing well below the β transition temperature.[97]

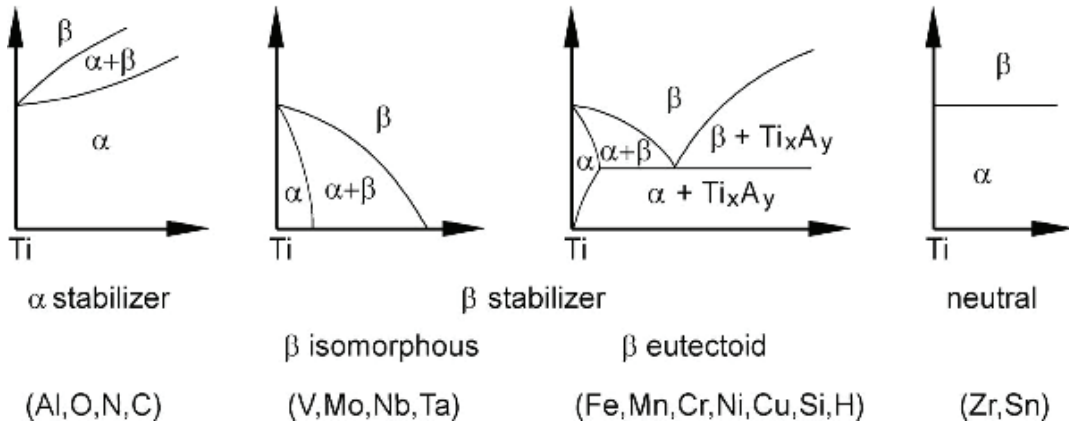


Figure 3.2: Schematic representation of the effect of alloying elements on titanium alloy phase diagrams.[97]

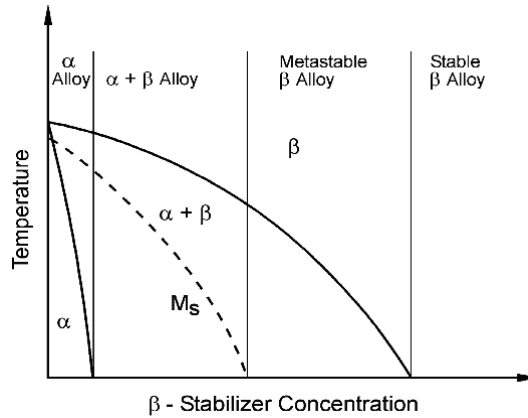


Figure 3.3: Pseudo-binary section through a β isomorphous phase diagram (schematically).[97]

β alloys contain one or more of the previously mentioned β stabilizing elements. They are typically characterized by high hardenability and formability but are prone to a

ductile-to-brittle transformation at low temperatures.[98] These alloys can have yield stress levels in excess of 1200 MPa if cooled quickly from the β phase field and aged in the temperature range of 500-600°C. For example, Bowen investigated the enhancement of the metastable β titanium alloy Ti-15Mo by altering the aging treatment of the alloy.[114] He found that a solution treatment at 725°C for 1 hour followed by aging for 16 hours at 475°C resulted in a yield stress of 1279 MPa. Peters *et. al.* also attempted to improve the yield strength of a metastable β titanium alloy, β -Cez (Ti-5.0Al-1.9Sn-5.5Zr-3.9Mo-2.2Cr-1.1Fe-0.1O, wt%).[115] This alloy had a yield stress of 1200 MPa when $\alpha + \beta$ processed at 870°C for 1 hour followed by a cool at 100°C/min. This cooling rate resulted in the precipitation of α plates. The samples were then annealed at 820°C for 1 hour, to coarsen the α plates, followed by cooling at 100°C/min. A final ageing was done at 580°C for 8 hours to precipitate fine α particles between the coarse α plates.[115] β alloys make up a relatively low share of the titanium commercial market but interest in these alloys is increasing due to their extremely high yield strengths. The majority of the commercial market is comprised of $\alpha + \beta$ alloys.

Alpha-beta alloys contain both α and β stabilizing elements in sufficient amounts to allow a retained mixture of α and β phases at room temperature. This dual-phase structure makes these alloys stronger than all α alloys and most of the metastable β alloys.

Additionally, their strength can be further enhanced by heat treating in a similar fashion to what was described previously for the metastable β alloys. However, the maximum heating temperature for the $\alpha + \beta$ alloys to improve strength is in the two-phase $\alpha + \beta$ region. This is in contrast with the metastable β alloys where the maximum heat

treatment temperature was in the β single phase region. This comparison is shown schematically in **Figure 3.4** where point **a** lies in the two-phase $\alpha + \beta$ region and point **b** lies in the single phase β region. If one were to anneal an $\alpha + \beta$ alloy in the single-phase β region (point **b** in **Fig. 4.4**) large β grains would form. Further age hardening would occur primarily at the grain boundaries and would not be distributed evenly throughout the alloy. This would result in a decrease of the mechanical properties of the alloy. Conversely, if an $\alpha + \beta$ alloy is heat treated in the two-phase region, the α grains present in the alloy will inhibit the growth of the β grains. If a quench is employed, the transformation of the existing β grains will be suppressed and upon subsequent aging, fine α precipitate particles may form in the β grains leading to enhancement of the mechanical properties of the alloy. Gunawarman *et. al.* found that a marked improvement in the fracture toughness of the $\alpha + \beta$ alloy Ti-5.5Al-3V-2Mo-2Fe could be improved by solution treating 850°C for 1 hour followed quenching and subsequent aging at 720°C for 1 hour followed by air cooling.[109] The phase diagram and heat treatment schedule for this work is shown in **Figure 3.5 a-b**. The solution treating temperature of 850°C (1123 K) is below the β transus temperature and well within the $\alpha + \beta$ two-phase region. Small α precipitates can clearly be observed in the prior β grains in the SEM micrographs of the resulting microstructure in **Figure 3.5 c**.

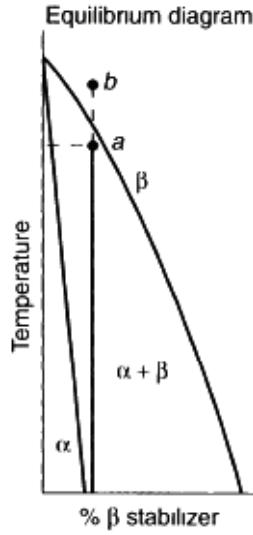


Figure 3.4: Schematic representation of the equilibrium diagram for an $\alpha + \beta$ titanium alloy.[98]

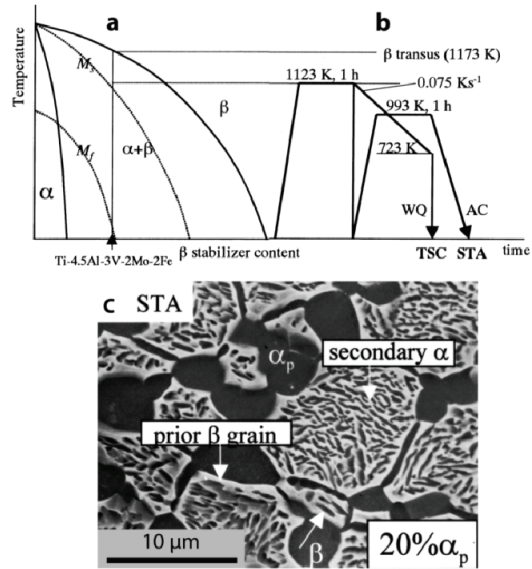


Figure 3.5: a) phase diagram of Ti-5.5Al-3V-2Mo-2Fe $\alpha + \beta$ alloy, b) heat treat schedule for the improvement of the fracture toughness of the alloy and c) SEM micrograph of the microstructure resulting from the heat treatment.[109]

The most widely used titanium alloy on the market to date is Ti64 (Ti-6wt%Al-4wt%V) an $\alpha + \beta$ alloy. It makes up 45% of the total commercial titanium market.[98] Because it contains both α and β stabilizing elements, Al and V respectively, its microstructure is comprised of both α and β grains and can be age hardened by heat treatment methods. Ti64 is extensively used in both the biomedical and aerospace industries for joint replacement[116], bone plates[117], screws for fracture fixation[118], dental implants[119], and turbine blades[120]. This is due to its excellent combination of its corrosion resistance and high strength and toughness. It is also relatively less expensive than wrought titanium and specialty titanium alloys due to its higher flexibility in design and increased yield.[121] According to Nastac *et. al.*, approximately 90% of all titanium castings are made of Ti64. Additionally, Ti64 is used in both property critical (i.e. cyclic fatigue in turbine blades[122]) and noncritical applications. Thus, materials that are rejected from the qualification process for the property critical applications can be sold for the non critical applications leading to less waste in the design process and a lowered overall cost of material design.[97]

The addition of alloying elements not only sets the phase fraction of α and β in a given titanium alloy, it also alters the kinetics and oxidation rates of the alloys. The following sections discuss some of the impacts alloying elements have on the diffusion in titanium alloys and the oxidation properties of the alloys.

3.4 Diffusion in Titanium

An understanding of the diffusion rates of both interstitial and substitutional alloying elements as well as self diffusion of titanium is important for a variety of processes. This

is because many of the processes used to tailor an alloys microstructure or properties, such as solution and aging heat treatments and recrystallization temperatures, are controlled by diffusion processes. Additionally, processes occurring during the service life of titanium part are also diffusional these include oxidation, hydrogen embrittlement and creep.[123]

The coefficients of diffusion for both titanium and alloying elements have been measured using a variety of methods including concentration gradient[124-128], Secondary Ion Mass Spectrometry (SIMS)[123], oxidation[129-138], stress-strain aging[124], and internal friction[137, 139, 140]. There is a wide range of scatter in the reported diffusion data. This is mainly due to the variety of testing methods employed in their investigation. Diffusion data is also commonly presented in terms of a pre-exponential factor D_0 and the activation energy Q . Using this information one can obtain the corresponding diffusion coefficient through the use of the Arrhenius law

$$D = D_0 e^{-Q/k_B T} \quad 3.1$$

where D is the diffusion coefficient of interest, D_0 is the pre-exponential factor, Q is the activation energy, k_B is the Boltzmann constant, and T is the temperature in degrees Kelvin. In the following sections a discussion of diffusion rates of different alloying elements in both the α and β phases of titanium is presented. Special attention is paid to the inter diffusion of aluminum and oxygen as well as the self diffusion of titanium to aid in understanding for later Chapters of this document.

3.4.1 Diffusion in α Titanium

Ti self diffusion in α titanium has been measured by a relatively small number of researchers compared to impurity diffusion. However, Mishin *et. al.* investigated Ti self diffusion in several CPTi samples with different impurity contents including an ultra pure specimen with very low impurity concentrations (Fe-0.02 ppm, Co-0.007 ppm and Ni-<0.015 ppm) to measure the effects these elements had on Ti self diffusion in the temperature range of 873-1133 K.[123] They found that the addition of impurities enhanced the self diffusion of Ti. They also looked at the impurity diffusion rates, specifically Al, using the same set of CPTi samples. They found that Al diffusion is a factor of 3-6 times slower than that of Ti self diffusion. Goold *et. al.* also studied the diffusion of impurities in α phase of titanium.[127] Of the impurities they tested (Al, Sn, V, and Mo), Al and Sn diffusivities were found to be dependent on concentration. Additionally, Al was reported to have the fastest diffusion rates of the impurities tested. Oxygen plays an important role in the phase stability of titanium. Titanium can absorb up to 33 at. % oxygen in solid solution. Oxygen is a strong α phase stabilizer that can be easily accommodated by the crystal in interstitial locations. Additionally, the diffusion of oxygen is reported to have a significant impact on the tensile properties of titanium.[137] Pratt *et. al.* studied the diffusion of oxygen in α titanium by internal friction methods.[140] They varied the oxygen concentration in the α titanium samples up to 5.5 at % and found a decrease in the diffusion rate with an increase in the oxygen concentration. Likewise, Miller *et. al.* used internal friction to measure the diffusion coefficient of oxygen over the temperature range of 300°C – 500°C.[137] They also noted a decrease in the diffusion rate of oxygen with an increase in concentration. These

results were somewhat contradicted by Unnam *et. al.* who used microhardness measurements on oxidized CPTi samples to calculate the oxygen diffusion coefficient in α titanium.[130] They found the oxygen diffusion coefficient to be independent of oxygen concentration over the concentration range of 1-10 at. %. This is one example of the discrepancies in the reported diffusion rates in the literature. However, these groups used significantly different measurement techniques and although the specifics of their findings differ the reported diffusivities for oxygen in α titanium are comparable. Rosa conducted a similar study to Unnam's where microhardness measurements of oxidized CPTi samples in the temperature range of 932°C to 1142°C were used to calculate the activation energies for oxygen diffusion in α titanium.[131] The reported findings were in close agreement to those of Pratt.

3.4.2 Diffusion in β Titanium

Similar studies for the diffusion rates of titanium, oxygen, and aluminum have been conducted for the β phase of titanium. Mishin *et. al.* found the self diffusion of Ti in β titanium to show a non-Arrhenius dependence with temperature.[123] This was attributed to a temperature dependence of the vacancy migration energy. They were able to compare the Ti self diffusion in β with their findings in α by using a generalized Arrhenius equation that took into account the temperature dependence of the vacancy migration energy.[123] It was reported that Ti self diffusion in β titanium is approximately two orders of magnitude faster than in α titanium. Goold *et. al.* reported on the diffusion of aluminum in β titanium measure by concentration gradient in alloys containing 2 and 12 at. % aluminum.[127] They found the diffusion rate of Al in both

alloys to be significantly higher than that of Ti self diffusion in the temperature range of 950°C to 1200°C. Diffusion of vanadium in this temperature range was also investigated and found to be an order of magnitude faster than that of aluminum.[127]

Oxygen diffusion in the β phase of titanium is of particular interest in many processes due to its influence on the formation of α titanium. The diffusion coefficient of oxygen in both α and β titanium phases was investigated by Rosa.[131] The reported findings showed a significantly higher activation energy for oxygen diffusion in β titanium (58.8 kcal/mole) than that of oxygen diffusion in α titanium (48.6 kcal/mol). However, when the diffusion coefficients for oxygen are calculated using the pre-exponential factors report by Rosa for the α and β phase (0.778 and 3.3×10^2 respectively), oxygen diffusion in β is shown to be more than an order of magnitude faster than in α . [131] Wasilewski *et. al.* utilized the oxygen concentration gradient developed in CPTi samples oxidized in the temperature range of 900°C – 1570°C in the presence of high purity oxygen to investigate the diffusivity of oxygen in β titanium.[132] They reported a D_o of 1.6 and an activation energy of 48.2 kcal/mol (+/- 3.2 kcal/mol) which is in good agreement with that of Rosa. Additional studies by other groups showed similar results for the diffusion of oxygen in β titanium. In all reports, oxygen showed faster diffusion rates in β than in α titanium.

Figure 3.6 shows a plot of selected diffusion rates of common alloying elements in both the α and β phases of titanium as presented by Lütjerin *et. al.*[97] Titanium self diffusion has several orders of magnitude faster diffusion rates in β titanium than in α . Similar results were observed for aluminum diffusion as well. The difference in the diffusivity of

oxygen between the two phases, while still faster in the β phase compared to α , is not as significant when compared to that of titanium self diffusion and aluminum inter diffusion. The diffusion rates for both hydrogen and iron are shown to be comparable in the two phases. While the effect of the different diffusion rates of alloying elements in the two phases is specific to the processes being controlled, it can have a significant impact. For example, the fast diffusion of hydrogen in both the α and β phases of titanium can have serious consequences for the application of titanium in certain environments due to the increased risk of hydrogen embrittlement.[97] Yeh *et. al.* reported on an increase in the subcritical crack growth (SCG) due to hydrogen embrittlement in Ti64 containing only 47 ppm of hydrogen.[141] Samples tested at an applied load of 40 and 50 MPa m^{1/2} exhibited completely brittle failure due to an autocatalytic process of hydride formation and cracking. The discrepancy in the diffusion rates of oxygen in the two phases also plays a role in the oxidation rate of each phase. The following section concludes the background discussion of titanium and its alloys with a brief look at its oxidation behavior.

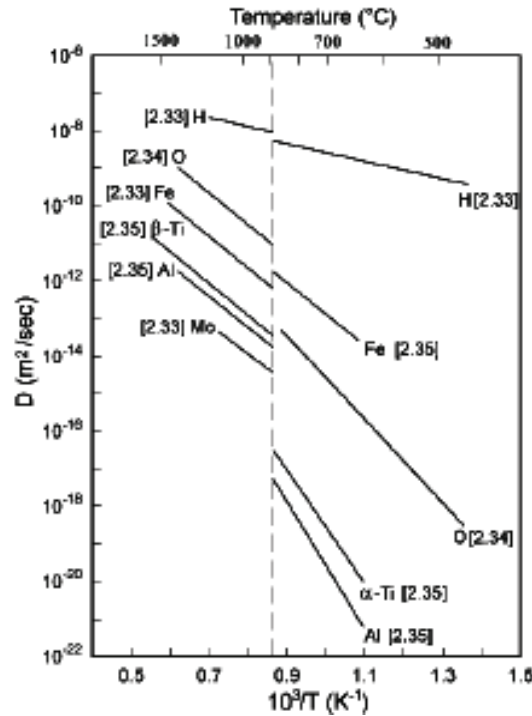


Figure 3.6: Selected diffusion rates of common alloying elements in both the α and β phases of titanium as reported in the literature.[97]

3.5 Oxidation

Titanium is chemically passive at low temperatures but when heated at elevated temperatures in the presence of oxygen an oxide layer forms, namely titanium dioxide (TiO_2). The thickness and structure of the resulting oxide layer is a function of both the oxidation temperature and oxygen environment. The diffusion coefficient for interstitial oxygen in titanium has been widely studied by both internal friction and oxidation routes as previously discussed. The diffusion coefficients for oxygen are not the same in both the α and β phases of titanium and thus the oxidation behavior is not the same.

Additionally, the adding of alloying elements can play an important role in both the oxidation rate and the resulting oxide composition. The following sections are devoted to

highlight some of these differences both in commercially pure titanium and in the most common titanium alloy, Ti6Al4V.

3.5.1 Titanium Dioxide

Titanium dioxide (TiO₂) is a semiconducting metal oxide. It has been widely used as a pigment in paints[142], a photocatalyst[31], a gas sensor[143], corrosion protective coating[144], and as an optical coating[145]. TiO₂ has three different major crystal structures; rutile, anatase, and brookite. However, only rutile and anatase play important roles in the previously mentioned applications. Both rutile and anatase have tetragonal crystal structures where $a = b \neq c$. The bulk crystal structures for these polymorphs are shown in **Figure 3.7**.

While TiO₂ is the most common form of titanium oxide it is not the only stable oxide that can form by the oxidation of Ti. **Figure 3.8** shows the Ti-O phase diagram over the temperature range of 0°C – 2000°C. Here, (Ti) α and (Ti) β refer to the α and β phases of titanium, respectively. The α phase can accommodate up to 33 at. % oxygen before forming TiO.₂[146] As more oxygen is consumed, several other oxide phases can form before TiO₂ including Ti₂O₃ and Ti₃O₅. However, these early forming oxide phases are rarely observed in the oxidation of Ti and its alloys at high temperatures (> 750°C). The oxidation products which form as a result of oxidizing titanium metal in air and in a variety of oxygen environments are discussed in the following section.

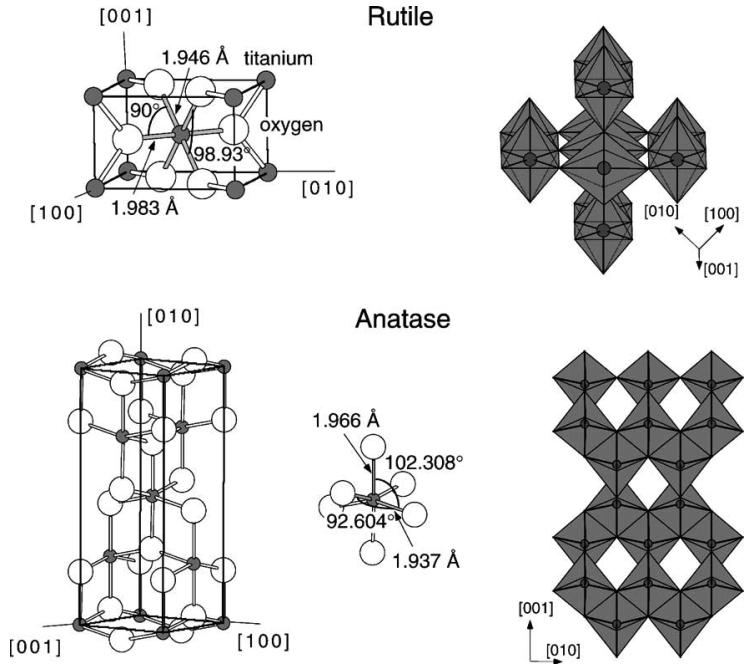


Figure 3.7 Bulk crystal structures for the tetragonal TiO₂ polymorphs rutile and anatase.[147]

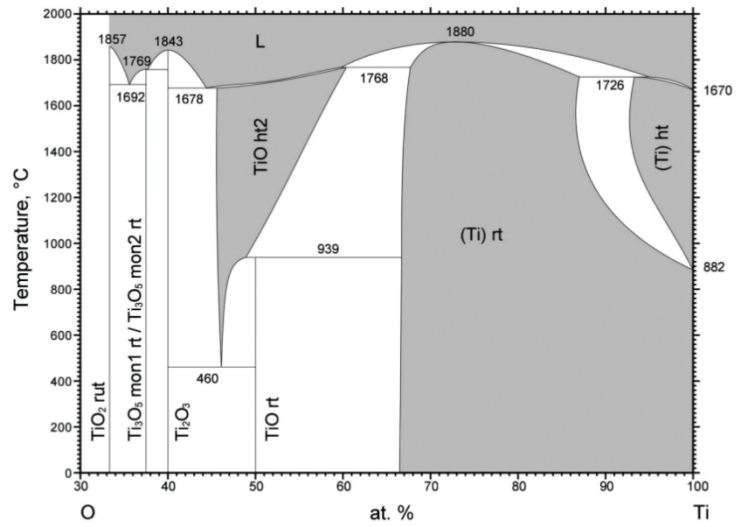


Figure 3.8 Binary phase diagram for the Ti-O equilibrium system.[146]

3.5.2 Commercially Pure Titanium Oxidation

While commercially pure titanium typically contains low levels of impurity atoms, a discussion of the role these atoms play in the oxidation of titanium is deferred to the following section. This section focuses on the oxidation of pure titanium. Early studies of the scaling behavior of titanium exposed to air at elevated temperatures were conducted by Morton *et. al.* over the temperature range of 500°C to 1300°C.[148] They reported only a rutile scale up to oxidation temperatures of 800°C after which TiO and Ti₂O₃ were reported at 825° and 850°C, respectively for extremely long oxidation times (< 100 hours). Kumar *et. al.* thermally oxidized CPTi in air to study the resulting oxide's corrosion resistance properties however their findings were contrary to those reported by Morton.[149, 150] Through XRD analysis Kumar observed both TiO and α titanium at an oxidation temperature of 500°C and TiO and rutile TiO₂ at 650°C.[150] An increase in the volume fraction of rutile with increasing oxidation temperature was reported.[149] At 800°C, the surface was reported to be completely covered with rutile grains oriented perpendicular to the substrate.[150] Gamelli *et. al.* examined the oxidation behavior of CPTi in air over the temperature range of 300°C to 750°C by differential thermal analysis (DTA), XRD, and thermogravimetry (TG). [151] They reported the formation of an amorphous passive oxide film at temperatures below 276°C. This film transformed into anatase TiO₂ above 276°C. At 444°C, the formation of rutile TiO₂ was observed. When oxidized in the temperature range of 457°C to 718°C, the oxide layer on titanium was shown to consist of both the anatase and rutile form of TiO₂ however, above 718°C the resulting oxide contained only the rutile phase. There are many conflicting reports on the structure and growth of the oxide layer on commercially pure titanium at temperatures

between 400°C and 700°C. However, most sources agree that above 750°C, only the rutile phase of TiO₂ is present in the resulting oxide.

A hard α -case has been reported to form on titanium during early oxidation of CPTi due to the uptake of oxygen into the surface layers of the titanium.[122, 152-158] The formation of the alpha case on titanium has been extensively studied by the casting community due to its impact on post casting processing. The alpha case can be formed not only by oxygen solid solution with titanium during oxidation but also by the uptake of other interstitial impurities including hydrogen and carbon.[158] This behavior has also been observed for titanium alloys containing both the α and β phases of titanium. Hongyan *et. al.* noted a distinct hardening effect of titanium alloys when exposed to oxygen at high temperature.[159, 160] Cross-sectional investigations of the oxidized alloys showed a much higher oxygen content in the α phase as compared to the β phase. Additionally, near the metal/oxygen interface the α titanium region increased in size and part of the β region transformed into α titanium which promoted further solid solution of oxygen.[159] This effect will be discussed in more detail in the following section. The α case developed by the uptake of interstitial atoms into the surface layers of titanium can be beneficial to mechanical properties such as hardness and strength[161] but can be detrimental in processes such as casting where further machining of the cast part are required and the presence of a hard α -case could lead to crack initiation and propagation.[158]

3.5.3 Oxidation of Titanium Alloys

The oxidation of titanium alloys is more complicated than that of commercially pure titanium due to the addition of alloying elements and their influence on oxide formation and oxygen migration in the metal. Additionally, it has been shown that the oxygen diffusivity is not the same in the α and β phases of titanium and as such one would not expect the oxidation rates to be the same. As a result, not only is the oxidation rate a factor of the alloying element content but also the ratio of α/β phase in the alloy. All alloys used in the studies presented in subsequent chapters of this document contain a significant amount of aluminum (at least 2 wt. %). As such, the alloys include in the following oxidation discussion will include aluminum. It should be noted that aluminum has an extremely high affinity for oxygen and several of the following referenced works discuss the formation of aluminum oxide (Al_2O_3) as a byproduct of the oxidation process. It should not be assumed that this is the case for all Ti alloys as several do not contain aluminum and therefore would not form Al_2O_3 upon oxidation at elevated temperatures. Commonly, alloying elements are added to titanium specifically to reduce its susceptibility to oxidation. However, not all alloying elements have a detrimental effect on the oxidation rate of titanium. In fact, several alloying elements actually enhance the oxidation kinetics in titanium. Chaze *et. al.* investigated the influence of aluminum, chromium, and silicon on the dissolution of oxygen in titanium during oxidation in both air and oxygen in the temperature range of 550°C and 700°C.[162] They found that both aluminum and silicon decreased the amount of oxygen dissolution in the metal while chromium had no notable impact. The reduction in oxygen dissolution was attributed to increased oxide formation in the presence of these alloying elements. Jung *et. al.* also

investigated the effects of Cr, in addition to Nb, Fe, and V, on the oxidation of titanium alloys at elevated temperatures.[163] All alloying elements investigated showed an improvement in the oxidation resistance of TiAl alloys as compared to the TiAl alloy without the additional elements. However, the increase in the wear resistance of samples alloyed with Nb improved dramatically compared to the other alloying elements investigated. This was attributed to an inhibition of grain growth in the protective oxide. A relatively small grain size was reported to retard the inward diffusion of aluminum from the protective oxide layer.[163] Xu *et. al.* noted similar improvements in the oxidation resistance of Ti-Ni alloys with the addition of Nb.[164] They attributed the increase in oxidation resistance to a complex Nb, Al oxide forming underneath a TiO₂ outer layer which resists the inward diffusion of oxygen and outward diffusion of metallic elements. Ion implementation of β stabilizing elements Fe, Mo, Ta, and W were also shown to improve the oxidation resistance of TiAl alloys.[165] All implanted elements showed improved oxidation resistance however the effect of Fe was less than the other elements investigated. The improvement was attributed to the formation of the β phase near the surface of the alloy resulting in an enrichment of Al in the outermost layer of the metal. This enhanced the formation of a thin but continuous Al₂O₃ layer at the metals surface which inhibited oxygen transport to the substrate. [165]

Oxidation of the Ti-6Al-4V alloy is of particular importance due to its abundant use in a variety of applications. Additionally, Ti64 is used extensively in studies involving nanowire growth by oxidation of titanium alloys presented in subsequent chapters in this document. As such, it is appropriate to discuss some of the relevant literature pertaining

to the oxidation of this ubiquitous alloy. Guleryuz and Cimenoglu investigated the effects of thermal oxidation of Ti64 at 600°C on the wear resistance of the alloy.[166] They found that oxidation at 600°C for 60 hours in air resulted in both a TiO₂ oxidation layer and a hard α -case underneath. Additionally, the resulting TiO₂ layer was shown to be comprised of both the anatase and rutile forms of TiO₂ though rutile was the dominant phase observed. Velten *et. al.* studied the results of thermally oxidizing Ti64 in laboratory air at 550°C and 600°C for 500 minutes by infrared (IR) spectroscopy and ellipsometry.[167] At these temperatures only the rutile form of TiO₂ was observed in the IR spectra of films measured to be 190 nm thick by ellipsometry. Additionally, a rapid increase in the oxide layer thickness with increasing time was observed after only 10 minutes for the alloys oxidized at 600°C compared to 550°C. A change from logarithmic growth to parabolic growth with an increase of oxidation temperature from 550°C to 600°C was reported.[167] Mungole *et. al.* also investigated the oxidation behavior of Ti64 in air but at temperatures in excess of 750°C.[168] Unlike the previously discussed reports, both TiO₂ and Al₂O₃ were reported forming during oxidation. The formation of Al₂O₃ in addition to TiO₂ on titanium alloys containing a significant amount of aluminum (> 2 wt. %) has been reported by many researchers however it is typically observed only in oxidation occurring at temperatures above 650°C or in alloys containing more than 20 wt. % Al.[156, 165, 169-174] Oxidation work presented in subsequent chapters of this document involves the oxidation of Ti64 in the temperature range of 700°C – 800°C. Thus, it is prudent to understand the expected oxide composition resulting from oxidation in this temperature range for Ti64. Du *et. al.*

conducted an extensive study of the structure of the oxide formed on Ti64 by oxidation in air in the temperature range of 650°C to 850°C.[171] Their work is consistent with the previously presented reports however it goes into greater detail as to the resulting oxide composition and structure. Oxidation experiments were performed in circulating air for up to 100 hours. **Figure 3.9** shows the surface morphologies of Ti64 samples oxidized in air at different temperatures. Nodular Al₂O₃ nuclei can be observed on the surface of all samples. At higher temperatures and longer oxidation times the Al₂O₃ grew laterally until a complete Al₂O₃ layer covered the sample with a TiO₂ layer underneath. XRD analysis showed only rutile TiO₂ and α-Al₂O₃ (corundum) present in the oxide layer. Cross-sections were taken of samples oxidized at 650°C, 750°C, and 850°C for 100 hours and examined by SEM and energy dispersive spectroscopy (EDS) to obtain the elemental distribution throughout these samples. Results of this analysis are presented in **Figures 3.10-3.12**. In each of the cross-sections an α-Al₂O₃ layer can be observed at the outermost (top in image) surface of the oxide scale. Additionally, a TiO₂ layer was observed at the oxide-metal interface for each of the samples. It was reported that the Al₂O₃ and TiO₂ scales grew alternately producing a multilayered structure. The number of the layers was dependant on the oxidation temperature and duration. Cracking was also observed between the alternating layers.

Du *et. al.* proposed a theory for the formation of the alternately layered structure and in the oxidized Ti64 samples.[171] TiO₂ forms first due to an increased activity in the presence of atmospheric oxygen. Once a thin TiO₂ layer is formed the alloy substrate is separated from its environment. This causes a reduction in the pO₂ at the TiO₂ substrate

interface to a value close to the dissociation partial pressure. The minimum aluminum activities at this partial pressure would be relatively high. Additionally, it was reported that vanadium suppresses the formation of Al_2O_3 in Ti64.[171] Thus, Al_2O_3 would be unlikely to form at the TiO_2 /substrate interface. At the oxide/gas interface the $p\text{O}_2$ would be substantially high thus reducing the minimum activity required to form Al_2O_3 though the formation of TiO_2 would still be thermodynamically favored. Both aluminum and titanium atoms would be diffusing outward from the alloy and oxygen would be diffusing inward. It is suggested that the diffusing oxygen and titanium would react at or near the TiO_2 /substrate interface effectively reducing the net flux of titanium through the oxide layer. However, this would not impede the diffusion of aluminum to the oxide surface. This would make it more kinetically favorable for an Al_2O_3 layer to form at the TiO_2 /gas interface.[171]

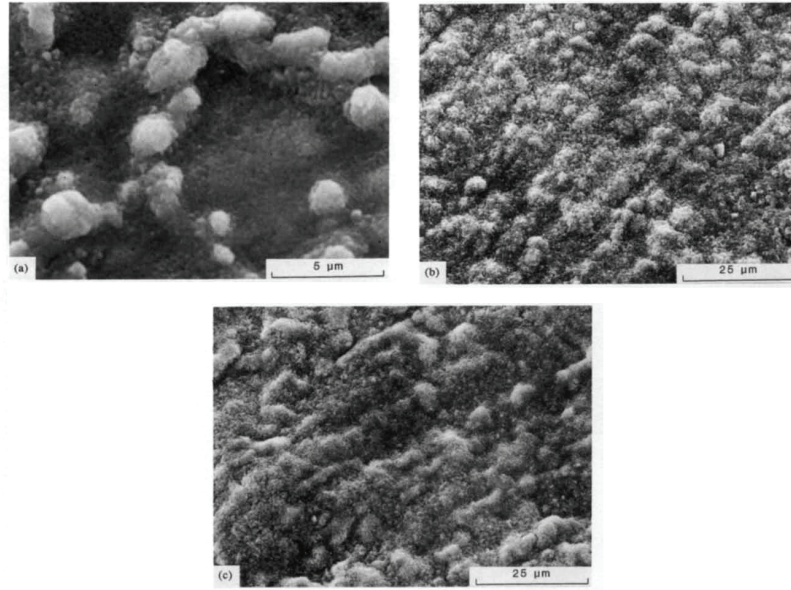


Figure 3.9: SEM micrographs showing the surface of Ti64 after oxidation in air at a) 650°C for 5h, b) 750°C for 100h, and c) 850°C for 100h.[171]

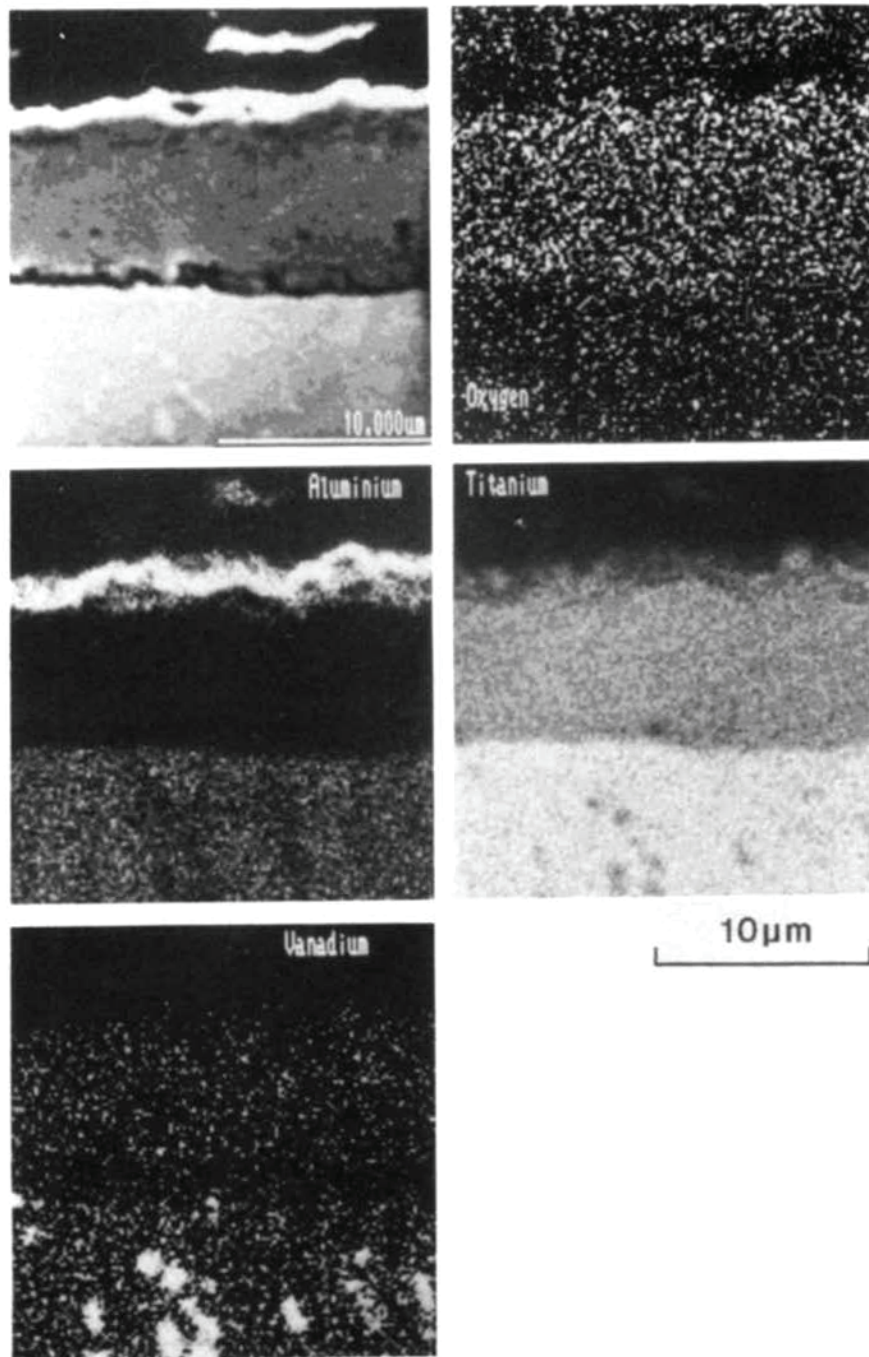


Figure 3.10: SEM image and accompanying compositional profiles through a cross-section of Ti-6Al-4V alloy after oxidation in air at 650°C for 100h.[171]

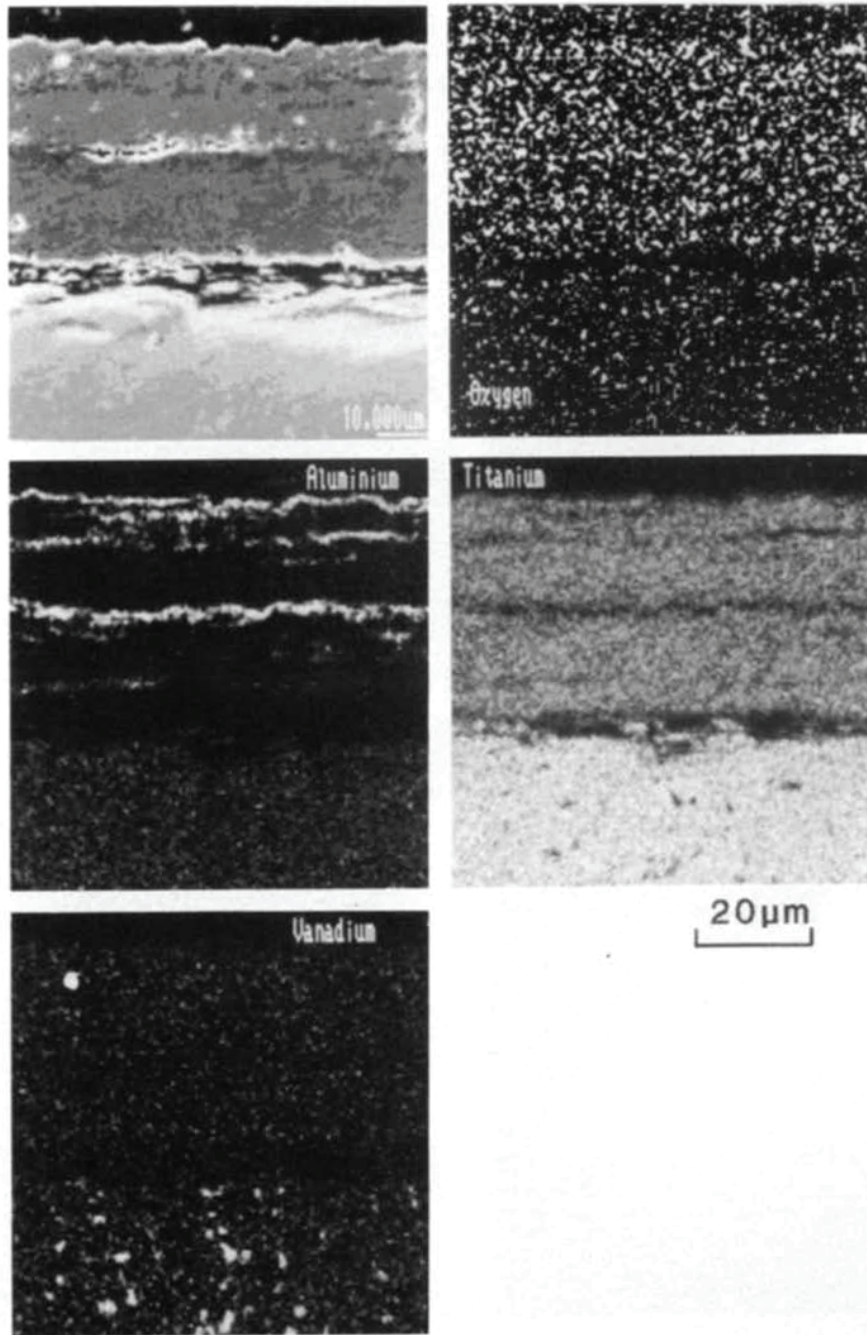


Figure 3.11: SEM image and accompanying compositional profiles through a cross-section of Ti-6Al-4V alloy after oxidation in air at 750°C for 100h.[171]

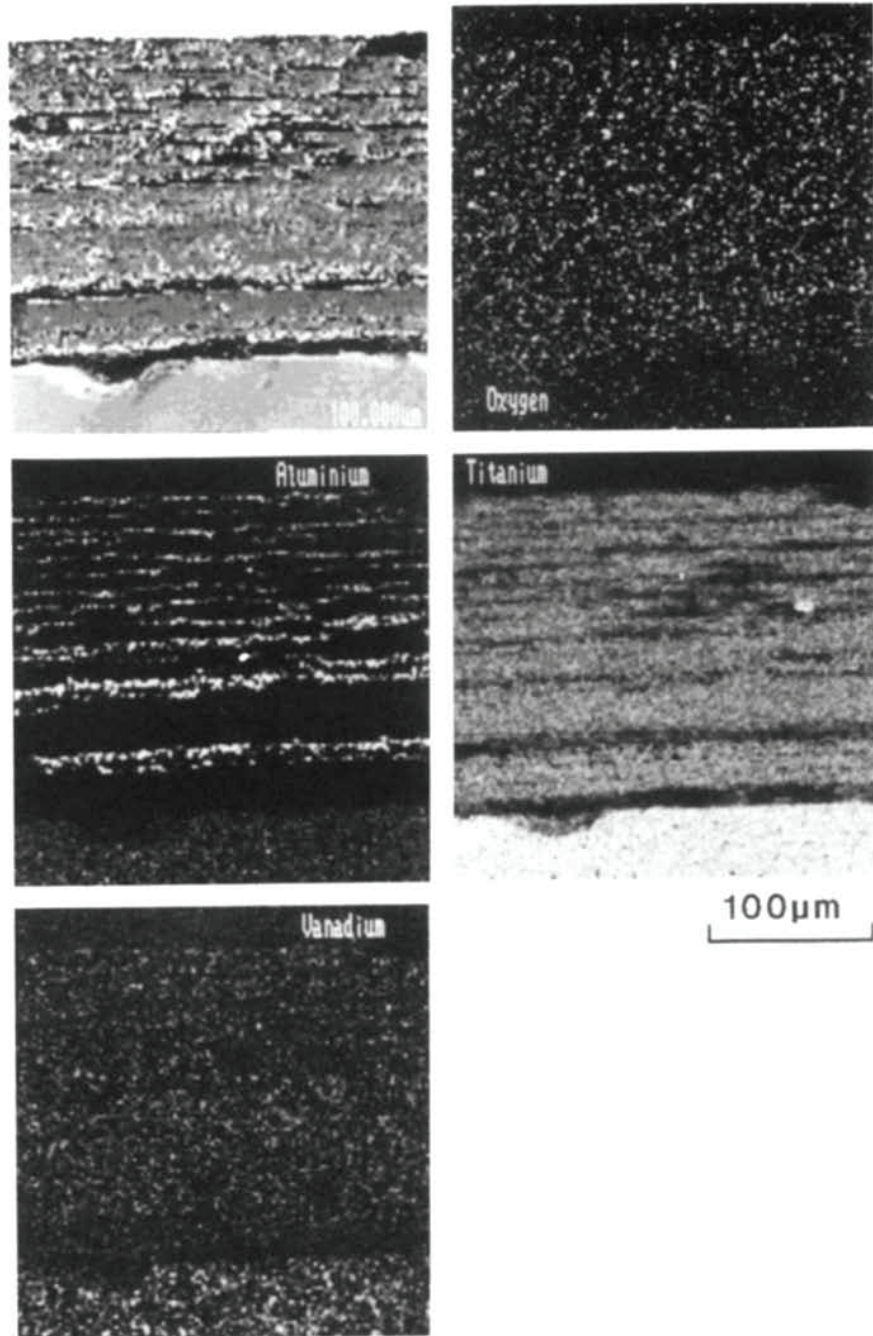


Figure 3.12: SEM image and accompanying compositional profiles through a cross-section of Ti-6Al-4V alloy after oxidation in air at 850°C for 100h.[171]

3.6 Summary

Titanium and its alloys are of significant commercial relevance due to their high strength to density ratio, excellent corrosion resistance, and biocompatibility. Titanium is currently being used for a wide range of applications ranging from turbine blades to dental implants. A brief listing of its more attractive properties were presented as well as a brief discussion of the impact of alloying elements on the phase stability in titanium. Alloy elements such as aluminum, oxygen, nitrogen, and carbon stabilize the α phase of titanium while molybdenum, vanadium, chromium, and iron stabilize the β phase of titanium by lowering the allotropic transformation temperature. Diffusion in titanium was shown to be dependent on the phase of titanium. Oxygen and aluminum, for example, were found to diffuse faster in β titanium than in α titanium. However α has a much higher solubility of oxygen (33 at. %) than β (4 at. %). Conversely, the diffusion of iron is faster in α titanium than in β . The oxidation behavior of both commercially pure titanium and titanium alloys containing aluminum were discussed. In CPTi, the oxide resulting from oxidation in air was a mix of both the rutile and anatase forms of TiO_2 . Additionally, the existences of both TiO and Ti_2O_3 in the resulting oxide were reported in the literature. The oxidation behavior of titanium alloys was much more complex due to the addition of alloying elements. Often, oxides comprised of both titanium and other alloying elements were observed. A detailed discussion of the oxide structure resulting from the oxidation of Ti64 in air as reported by Du *et. al.* was presented as a platform for later discussions in this document. Subsequent chapters will build on the background information presented in this chapter.

Chapter 4: Growth of TiO₂ Nanowires on Ti Alloys

4.1 Background and Previous Work

A low cost one-step heat treatment process has been developed to produce nanowires (NWs) of titanium dioxide (TiO₂) by thermal oxidation of titanium alloys. This chapter is focused on a discussion of the growth process, the identification and optimization of the governing growth parameters, and the influence they have on the resulting sample morphology. All discussion pertaining to the mechanisms governing the growth of 1-D structures by oxidation is reserved for the next chapter.

The general growth process used to produce 1-D TiO₂ NWs on Ti alloy substrates is straight forward and proceeds as follows. A cut, polished (1200 grit), and cleaned Ti alloy sample is placed into a horizontal tube furnace and heated to the desired annealing temperature under flowing argon. The sample is held at this temperature for a given duration after which the sample is cooled and removed from the furnace for characterization. **Figure 4.1** is a typical example of NWs produced by this process on a titanium alloy substrate. This process was previously discovered by Dr. Huyoung Lee, a former student in the Department of Materials Science and Engineering at The Ohio state University, and discussed extensively in his doctoral thesis.[175] The following discussion highlights some of his more significant findings in process development and optimization.

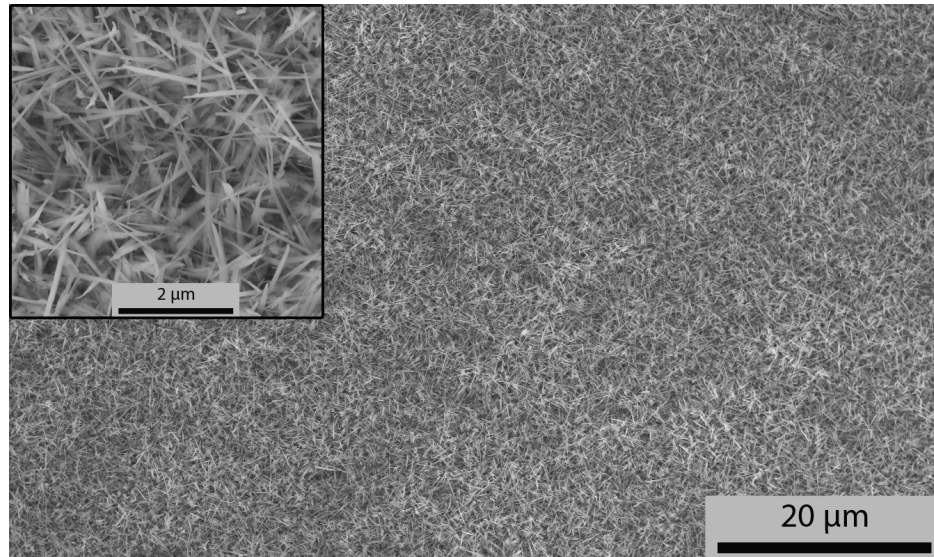


Figure 4.1: SEM micrograph of typical NWs produced by the oxidation of Ti alloys in a low oxygen environment.

NW growth occurred on both commercially pure Ti (CPTi) and Ti alloy substrates however, the most abundant NW growth was observed on the Ti alloy substrates, specifically Ti-6 wt% Al-4 wt% V (Ti64) and Ti-5 wt % Al- 5 wt % V-5 wt % Mo -3.5 wt % Cr-0.5 wt % Fe (Ti5-5-5). CPTi showed only very short NWs under the typical processing variations. A discussion of possible reasons for this discrepancy in NW production is reserved for Chapter 5 and an alternative process to increase the NW yield on the CP Ti substrates is presented in Chapter 6 of this manuscript. The wires grown on the Ti alloy substrates were identified to be rutile TiO_2 by x-ray diffraction (XRD) analysis. The majority of the NW characterization was done via scanning electron microscopy (SEM) where the NW lengths and diameters were directly measured. Very little transmission electron microscopy (TEM) was performed on the NWs. The limited TEM work that was done showed the NWs to consist of both a core and a shell. This

pared with electron dispersive spectroscopy showed the core to be rich in Ti and the shell to be rich in Al. *However, no structure was identified for either the core or the shell.*

SEM analysis showed the length and diameter of the NWs varied depending on the growth parameters used to produce them. The effects of these parameters as presented by Lee are discussed briefly in the following paragraphs.[176]

Three parameters governing the oxidation of Ti alloys to produce NWs were extensively investigated; annealing temperature, annealing duration, and gas flow rate. During the individual investigation of each of these parameters the other two parameters were held constant.

It is well known that the temperature at which a metal is oxidized can have a profound impact on the resulting oxide.[165-168, 171] For this reason, temperature was thought to be one of the critical growth parameters. To investigate the impact the oxidation temperature had on the resulting NWs, several experiments were conducted in which the temperature was increased from 600°C to 900°C in 100°C increments in 500sccm flowing Ar for the duration of 8 hours with a furnace ramp rate of 23°C/min.[175]

At temperatures near 600°C only very short NWs, with lengths of approximately 500nm, formed. However when the temperature was increased to 700°C, all other parameters being constant, NWs with lengths in excess of 3 μm grew. As the temperature was further increased to 800°C, a mixture of well defined NWs and larger faceted crystals grew.

When the annealing temperature was as high as 900°C only large, faceted crystals formed. This trend in NW growth variation with temperature was found to be consistent with both the Ti64 and Ti-555 alloy systems. Based on these results, Lee chose 700°C as

the optimum annealing temperature to produce a high density of NWs with sufficient lengths. [175]

The rate at which Ar was allowed to flow into the reaction chamber was also thought to play an important role on NW formation. To investigate this, samples were heated to 700°C at a furnace ramp rate of 23°C/min and held at this temperature for 8 hours. The flow rate of the Ar gas was varied from 250 sccm to 1000 sccm to see its impact on the resulting NW morphology. At 250 sccm a high density of NWs was observed with lengths of 2-5µm and diameters of 70-150nm. When the flow rate was increased to 500 sccm, the average NW length did not change however the range of NW diameters decreased to 35-130nm. As the flow rate was further increased to 1000 sccm, this trend continued with the NW diameters decreasing to 20-70nm.

Flow rate was found to play a negligible role in the formation of NWs. The length and density of the NWs remained relatively constant over a range of flow rates, only the diameters were affected. 500 sccm was chosen as the optimal flow rate due to its favorable balance between NW coverage, length, and diameter and the conservation of Ar gas.[175]

Lee also investigated the annealing duration which he defined as the length of time at which a given sample was oxidized at an elevated temperature.[175] The annealing duration was optimized to strike a balance between the NW's length and coverage while minimizing the time required operating at high temperature. The following procedure was used for all experiments: 1) ramp to 700°C at 23°C /min under 500 sccm of flowing Ar, 2) hold at 700°C under 500 sccm flowing Ar for a given time, 3) remove the sample from

the furnace after the desired annealing duration effectively air quenching the sample. For very short oxidation times, less than 30 min, Lee found that no NWs formed and only an oxide scale with nano-sized islands observed via SEM. As the oxidation time increased, short NWs with relatively low sample coverage emerged. After an annealing duration of 1 hour, the coverage of NWs remained fairly constant and only their lengths increased. The increase in the length of NWs was relatively constant as time increased. This growth rate was calculated to be approximately 300 nm per hour for oxidation at 700°C under 500 sccm of flowing Ar. An annealing duration of 8 hours was chosen as the optimum oxidation time due to the growth of reasonably long NWs (~2.5 μm) in a relatively short period of time.

Given the discrepancy of NW growth between the CPTi and the Ti alloy substrates discussed previously, it was prudent for Lee to investigate what role, if any, the alloying elements played in the growth of the NWs.[175] In the two main alloys used in his study, Ti 6%Al-4%V and Ti 5%Al-5%V-5%Mo-3.5%Cr-0.5 %Fe, both Al and V were common. Additionally, in Ti 5-5-5, Mo was also a predominant alloying element. To investigate the impact each of these three alloying elements had on NW formation, binary alloys were oxidized under the standard conditions and their resulting oxides were characterized.

Lee found that no NW growth occurred on the Ti-V and Ti-Mo binary alloy samples.[175] Only small (~100nm) faceted crystallites formed. The Binary Ti-Al alloy did show NW growth although the resulting NWs were quite small and occurred at a much lower density than the Ti64/Ti5-5-5 alloy counterparts. It was concluded that Al

played a critical role in the growth of the TiO₂ NWs while Mo and V played little to no role in NW formation. It was also concluded that the best alloy compositions for the growth of NWs by this process contained both Al and V.

It is important to keep in mind that these different alloying elements play important roles in the alloys themselves. Both of these alloys (Ti64 and Ti5-5-5) are of mixed phases, α (hcp) and β (bcc). Unalloyed Ti exists in the α phase at standard temperature and pressure. The metal goes through an allotropic phase transformation to β at approximately 882°C. The addition of alloying elements can either increase or decrease the transformation temperature. An alloying element that lowers the transition temperature making the β phase stable at lower temperatures is known as a β -stabilizing element. Both V and Mo fall into this category as does Cr. Conversely, Al is an α stabilizing element, thus it raises the transition temperature between α and β . A preference for NW growth on β titanium was observed by Lee on several as-received Ti5-5-5 samples. To investigate this phenomenon, Lee oxidized a near α (Ti-7Al-2V), an $\alpha + \beta$ (Ti64), and a β (Ti5-5-5) alloy and characterized the resulting NW growth by SEM.[176] Large clumps of relatively long NWs formed surrounded by large areas of limited NW coverage. The α -phase is not devoid of NWs but in fact has very small NWs growing across its surface. The Ti685 microstructure can be described as islands of β in a sea of α , while Ti64 is closer to an even mixture of α and β , and Ti5-5-5 can be described as islands of α in a sea of β . By comparing growth on all three of these Ti alloys Lee concluded that the preference for NW growth on β was apparent and could not be ignored.[175] As such, alloys with a majority β -phase were recommended for NW

growth. Lee suggested possible reasons for the β -phase preference. These suggestions along with new insights are presented in Chapter 5 of this manuscript.

The three growth parameters previously investigated were annealing temperature, duration, and gas flow rate. Of these, the annealing temperature was identified to have the greatest impact on NW morphology with the optimum temperature said to be near 700°C. The annealing time dictated the ultimate length of the NWs however, a sufficient duration of annealing was necessary to initiate the NW growth. The gas flow rate was found to have a comparatively negligible effect on NW formation only slightly adjusting the resulting diameters. However, the impact of the flow rate on NW diameter was significantly less than that of temperature. The impact of Ti alloy composition was also investigated. It was concluded that of the alloying elements Al was required for a high NW yield on alloy samples and alloys containing both Al and V produced the most abundant formation of NWs after oxidation. The NW growth also showed a preference for the β -phase of the Ti alloys.

While Lee conducted a rather comprehensive study of the parameters governing the production of NWs by oxidation of Ti Alloys in an oxygen deficient environment there is an important parameter that was overlooked, the oxygen concentration during oxidation. Oxygen concentration is known to have a significant impact in the oxidation behavior of metals.[87, 177] Additionally, the application of this technique to produce NWs on Ti alloys was focused solely on bulk material. To use this process in a wide range of applications a transfer of this technology to other substrate configurations is desirable. There have been recent advances in both of these areas, investigation of the effects of

oxygen during oxidation and transfer to new substrate configurations, as well as a more in depth characterization of the NWs themselves. The remainder of this chapter focuses on recent contributions to the growth of TiO₂ NWs on Ti alloys.

4.2 Experimental

Commercially pure Ti (Ti Foil 99.99%+, Alfa Aesar), Ti64 (grade 5, Ti-6 wt % Al- 4 wt % V; Onlinemetals, Seattle, WA), Ti5-5-5 (Ti-5 wt % Al- 5 wt % V-5 wt % Mo -3.5 wt % Cr-0.5 wt % Fe) bars prepared in house, were used for the bulk Ti experiments.

Powders of CPTi (Ti powder –325 mesh 99.98%, Sigma Aldrich), Ti64 (Ti-6Al-4V -170 + 325 mesh, Powder Alloy Corporation, Ohio), and Ti5-5-5 (prepared in house by atomization) were also used. Bulk samples were cut using a diamond cutter (LECO, part number 801-136) and mechanically polished using SiC sand paper (1200 grit). After polishing, all samples were cleaned by the following procedure including a rinse in deionized (DI) water between each step: 1) 5 min ultrasonication in acetone, 2) 5 min ultrasonication in methanol, and 3) 5 min ultrasonication in DI water. The samples were inserted into a quartz tube (OSU Glass Shop) which was then placed in a horizontal tube furnace (Lindberg, TF55035A) for gas heat treatments. The oxidation environment was set by flowing the desired gas or gas mixture at a target flow rate maintained by a digital flow meter(s) (C100L, Sierra Instruments) while the oxygen partial pressure in the gas was monitored by an oxygen sensor (ZRO2000, Alpha Omega Instruments). The furnace temperature and gas flow rate were computer controlled through an instrument control and data acquisition LabView program written in-house. The oxygen concentration was

converted to a current by the oxygen sensor, monitored by a data acquisition system (34972A, Agilent) and read into the LabView program for collection and display.

A Sirion SEM (FEG-SEM, Model Sirion, FEI, Oregon) was used for high resolution observation to detect changes in the surface morphology of the specimens at sub-micron scales. Prior to SEM characterization, samples were coated in a thin layer of Au using a sputter coater (Model 3 Sputter Coater 91000, PELCO) at a plasma current of ~15mA for 40 seconds. Crystal structure verification was performed using XRD analysis (Scintag PAD-V and Bruker XD) prior to Au coating. The structure of the resulting NWs was examined with a transmission electron microscope (TEM, Model CM200, FEI).

Elemental analysis of individual NWs was performed by electron dispersive spectroscopy (EDS) in a high resolution TEM (HRTEM, Model TF20) operating in the scanning mode. The NWs were collected on a lacy carbon coated copper TEM grid by scraping the specimen a razor blade and dispersing in ethanol. Droplets of the nanowire containing solution were placed on a carbon-coated copper grid and dried at 40°C in a drying oven (Lindburg, M01430A).

4.3 Results and Discussion

4.3.1 Nanowire Morphology and Phase Identification

The vast majority of Lee's characterization and optimization of NW growth on titanium alloys was conducted on Ti5-5-5 due to its high phase fraction of β titanium.[175]

However, no titanium alloy is more widely employed than Ti-6Al-4V. As such, the vast majority of the work presented throughout the remainder of this chapter focuses on NW growth by oxidation of Ti-6Al-4V in a low oxygen environment. NWs produced by the

oxidation of Ti-6Al-4V were characterized by SEM, XRD, and TEM analysis. Samples were oxidized in laboratory grade Ar at a flow rate of 500 sccm at 700°C. Typical experiments utilized an 8 hour oxidation treatment in this environment with a 23°C/min heating rate and furnace cooling to room temperature.

Figure 4.2 shows an SEM image of a typical nanostructured surface of Ti64 resulting from oxidation under the afore mentioned conditions. Well defined NWs with diameters less than 100 nm and lengths of 2-7 μm were observed. **Figure 4.3** is an SEM image taken at the edge of the sample presented in **Figure 4.2**. Here, individual NWs with lengths in excess of 5 μm are clearly visible. One can also observe the high density of NWs formed on the alloy surface by the oxidation process.

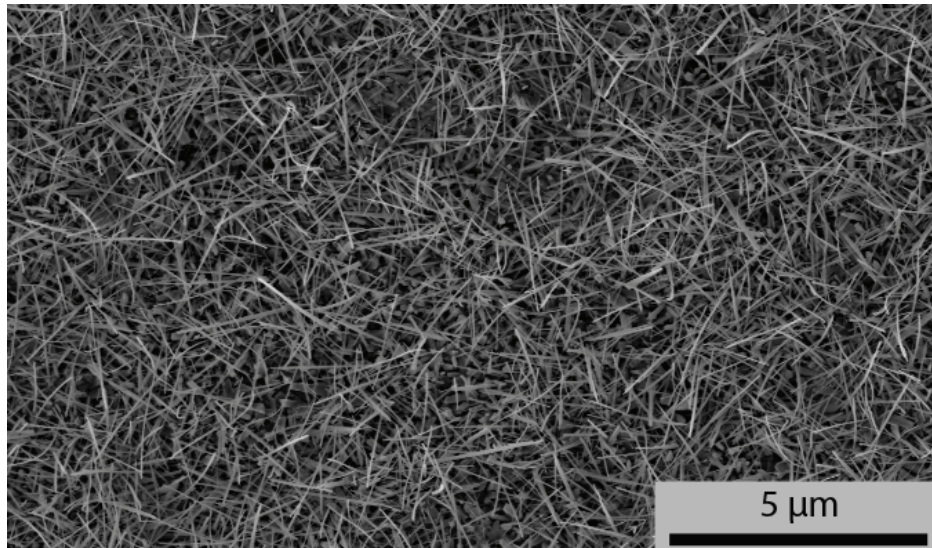


Figure 4.2: SEM micrograph showing typical nanostructured surface resulting from the oxidation of Ti-6Al-4V at 700°C for 8 hours in 500 sccm of laboratory grade Ar.



Figure 4.3: SEM image taken at the edge of the oxidized Ti64 sample shown in **Figure 4.2**.

The substrate morphology played an important role in the resulting NW coverage. As mentioned in the previous work section of this chapter, there is a strong preference for NW growth to occur on the β phase of titanium. Ti64 being an $\alpha + \beta$ titanium alloy has a near even ratio of the two phases with slightly more α than β . The Ti64 sample oxidized for **Figure 4.2** and **Figure 4.3** was heat treated in such a way as to equally distribute the beta phase throughout the sample. **Figure 4.4** is an SEM image of an as-received Ti64 sample after oxidation. The as-received sample contained globular β titanium surrounded by an α matrix. The impact of the microstructure prior to oxidation is clearly evident in the resulting NW distribution on the sample. To further confirm that this was a result of the parent microstructure prior to oxidation, a Ti64 sample was subjected to a heat treatment to produce a Widmanstätten microstructure. To create the microstructure, a piece of Ti64 was heat treated in a reducing environment, to minimize oxidation, at

1000°C for 3 hours and allowed to cool to room temperature. An optical micrograph of the resulting structure is shown in **Figure 4.5 A**. This alloy was then oxidized under a limited supply of oxygen and extensive NW growth was observed on the β lathes while limited growth was observed on the α matrix. A low magnification SEM micrograph of the resulting sample is shown in **Figure 4.5B**, **C** and **D** are high magnifications of the α and β regions, respectively. Throughout the sample a preference for growth to occur on the β -phase was evident.

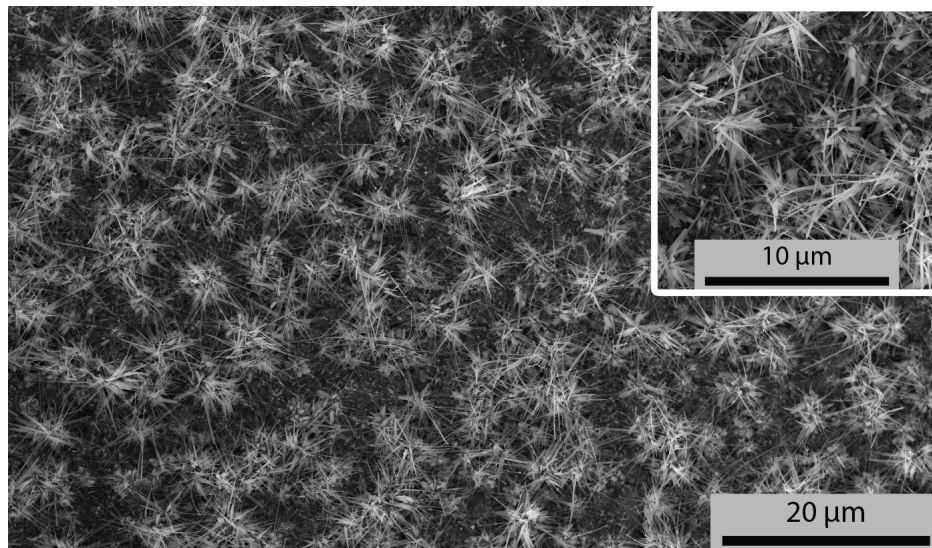
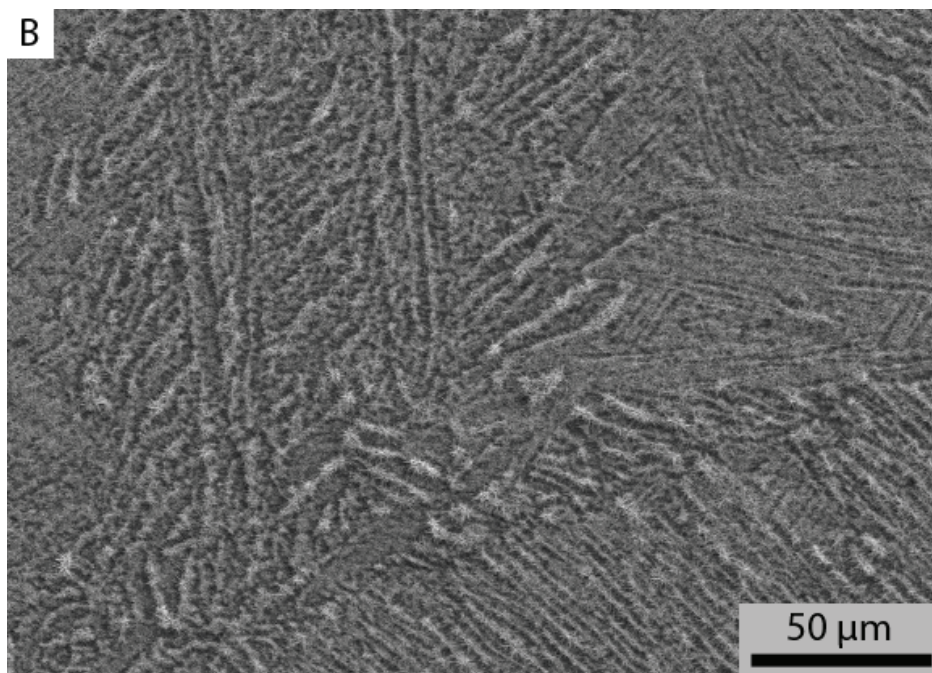
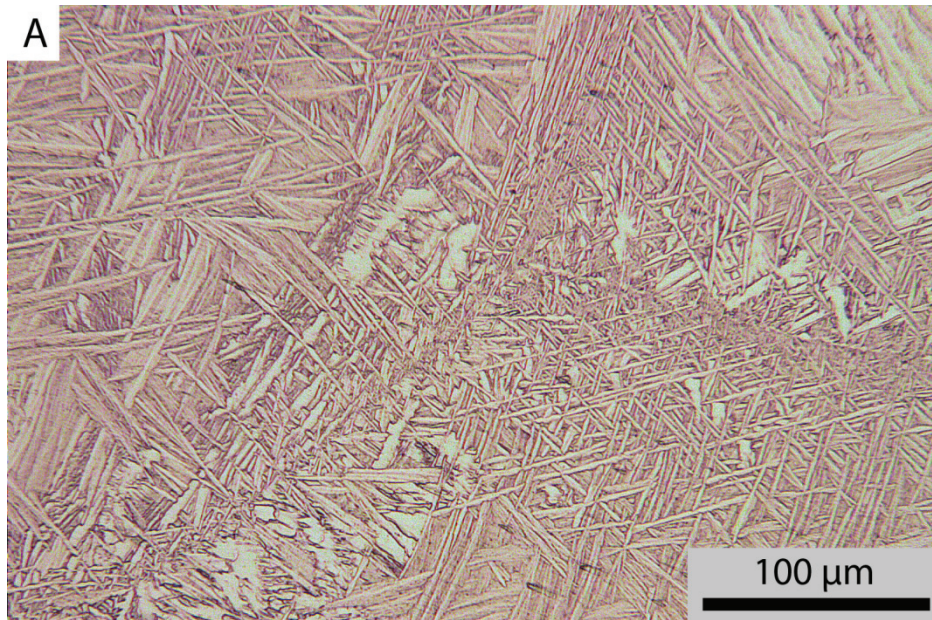


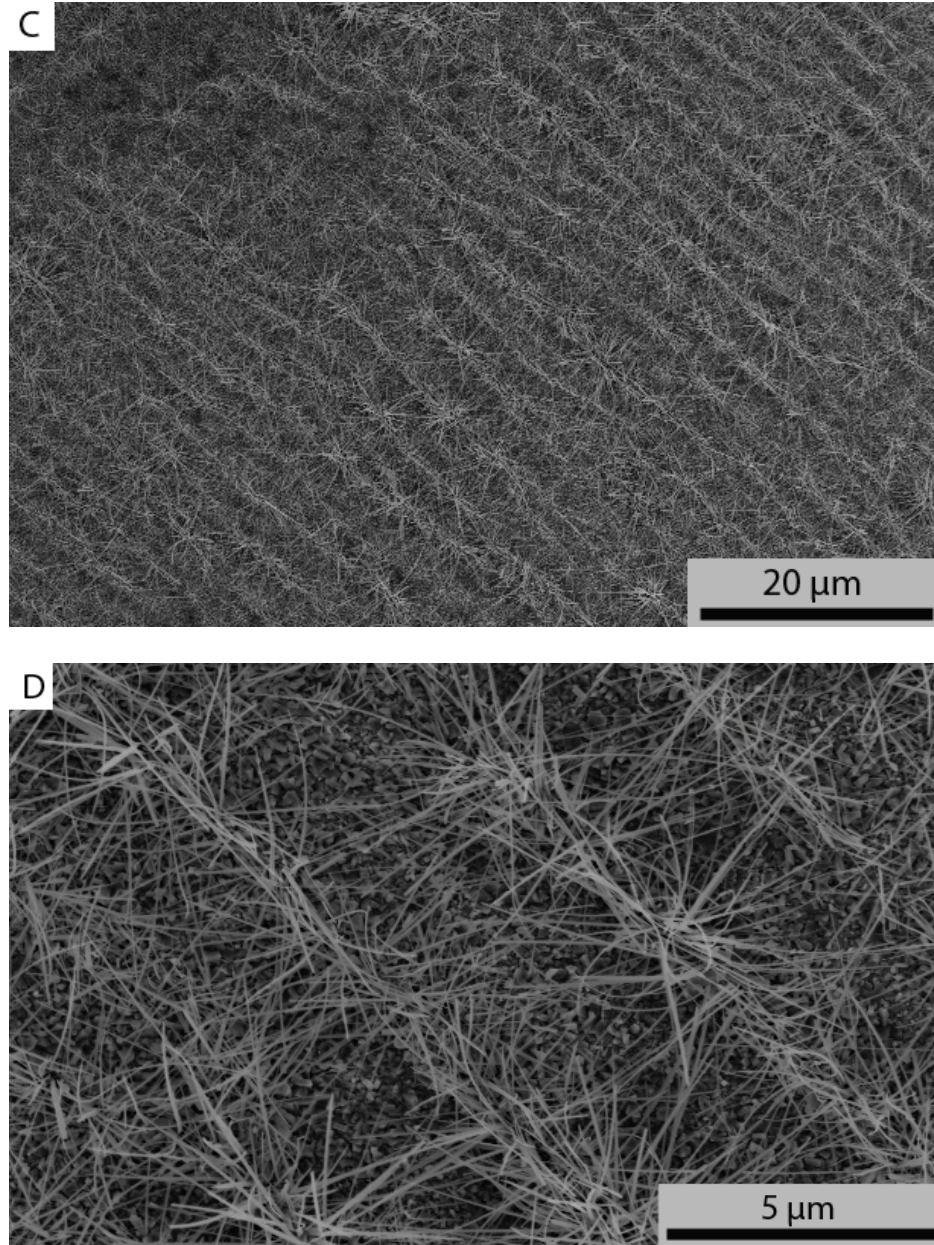
Figure 4.4: SEM image of an oxidized sample of as-received Ti64 containing globular β titanium in an α matrix. Inset shows higher magnification of the distribution of phases.



continued

Figure 4.5: A) An optical micrograph showing Widmanstätten grain structure of polished Ti64 and SEM micrographs showing B) low magnification and C) and D) high magnification images of preference for NWs to grow on the beta lathes of columnar Ti64.

Figure 4.5: continued



XRD analysis of the Ti64 samples was performed before and after oxidation (**Fig. 4.6**). Before oxidation a mixture of both the α and β titanium phases were evident in the resulting pattern. After oxidation at 700°C for 8 hours a mixture of rutile TiO_2 , corundum

(Al₂O₃), and α titanium were observed. The presence of CaCO is a result of the clay used to mount the sample for XRD analysis. The presence of corundum was not altogether unexpected as it has been widely reported as a corrosion and oxidation inhibitor in Ti64.[105, 171] However, where it resides in the nanostructured morphology resulting from this oxidation process and what role it may play in NWs formation was unknown.

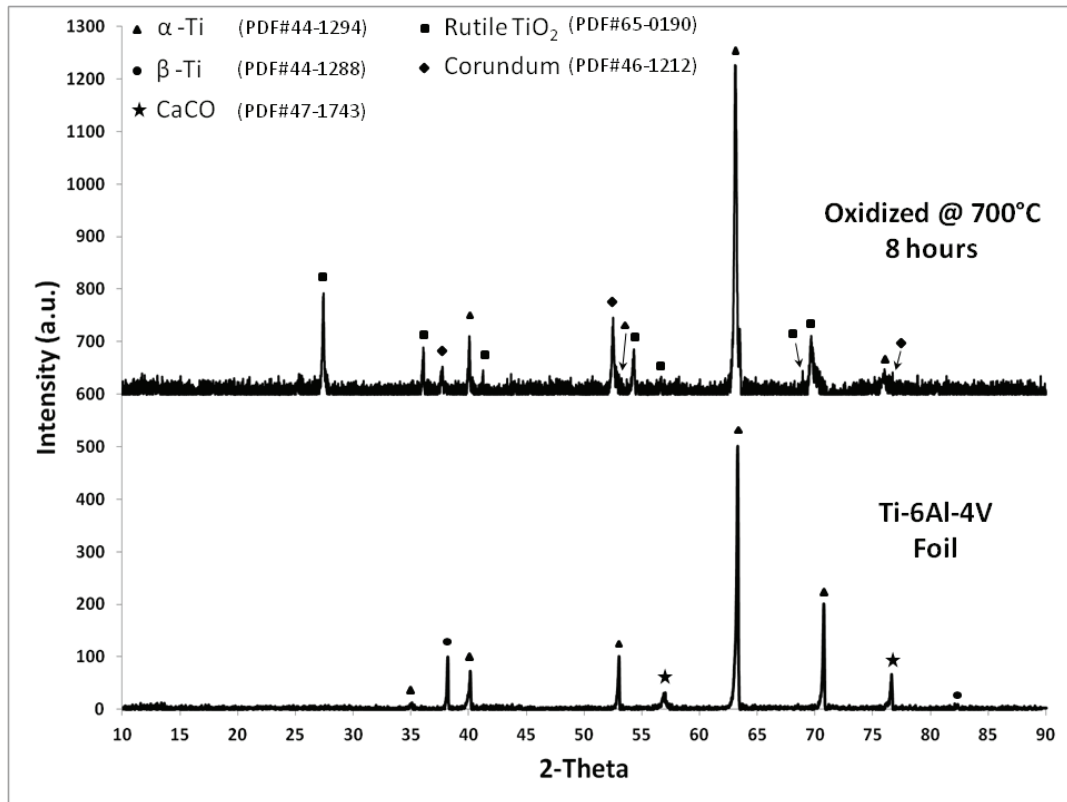


Figure 4.6: XRD analysis of Ti64 foil as received and oxidized at 700°C for 8 hours.

Recently, TEM analysis was performed on the NWs grown on Ti64 to investigate the possible incorporation of corundum in the NW structure. To create the TEM samples, a piece of Ti64 was oxidized at 700°C for 8 hours. After which, the NWs were scraped off

into an ethanol solution and sonicated for 5 min to disperse them in the solution. Several drops of the solution were then placed on to a lacy carbon grid and allowed to dry.

Figure 4.7 A shows a bright field (BF) TEM image of multiple NWs on a lacy carbon grid. Each of the two wires (marked 1 and 2 in the image) are approximately 80 nm in diameter and although the magnification is too high in this image to see, each of the wire segments were roughly 2 μm in length. The wires marked 1 and 2 in the image were selected for further investigation and characterization.

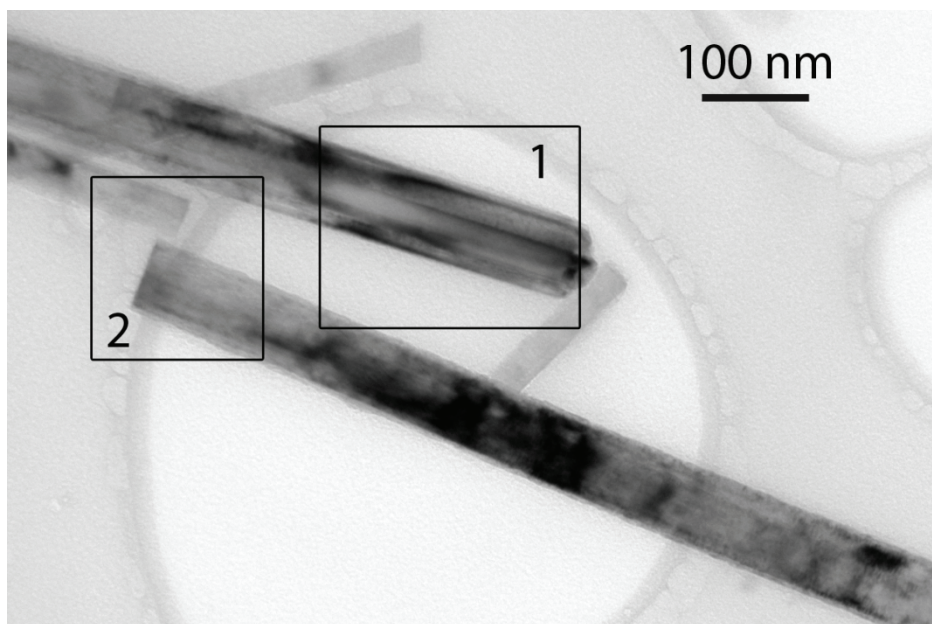


Figure 4.7: Bright Field (BF) TEM image of NWs grown on Ti64 substrate. Areas marked “1” and “2” were selected for further characterization.

A higher magnification of wire “1” is shown in **Figure 4.8**. In this image a distinct layering of the NW is visible. The inner core layer is approximately 36 nm in diameter and appears to have a uniform diameter along the length of the wire. The outer shell layer

does not appear to be symmetric in this image with one side being more than twice the width of the other. The selected area diffraction (SAD) pattern for this wire is displayed in the inset in **Figure 4.8** and shows the diffracting portion of the wire to be rutile TiO_2 . The diffraction pattern has a zone axis of $[100]$. The core of the wire appears to be smooth and made up of one individual structure while in the shell what appear to be multiple nano-sized grains are observed. Additionally, the NWs' growth direction is aligned with the $\langle 002 \rangle$ family of \mathbf{g} vectors as observed in the SAD inset in **Figure 4.8**. Unfortunately, no dark field (DF) imaging of this NW was performed using low index \mathbf{g} -vectors from the $[100]$ pattern due to time constraints and instrumentation issues. This work should be completed to identify exactly which portion of the imaged specimen is contributing to the diffraction pattern. Additionally, this would confirm if the core, shell or both, whichever is contributing to the diffraction pattern, is the rutile phase.

The wire labeled "2" in **Figure 4.7** was also imaged at higher magnification in BF mode as shown in **Figure 4.9 A**. The core-shell morphology is not as visible in this wire as it was in wire "1". The corresponding SAD pattern for this wire (**Fig. 4.9 B**) shows 2 distinct patterns. Neither of these patterns are completely on zone however they were able to be indexed to a $[100]$ rutile and $[0001]$ corundum zone axes. The intensity of the two diffraction patterns is nearly equal indicating that each crystal structure is contributing equally to the contrast in the BF image. This could account for the lack of a clearly defined core-shell interface in the image. However, one can almost make out a change in contrast indicating the core-shell interface as indicated by the white arrows in **Figure 4.9 A** though an argument could be made that they are simply thickness fringes.

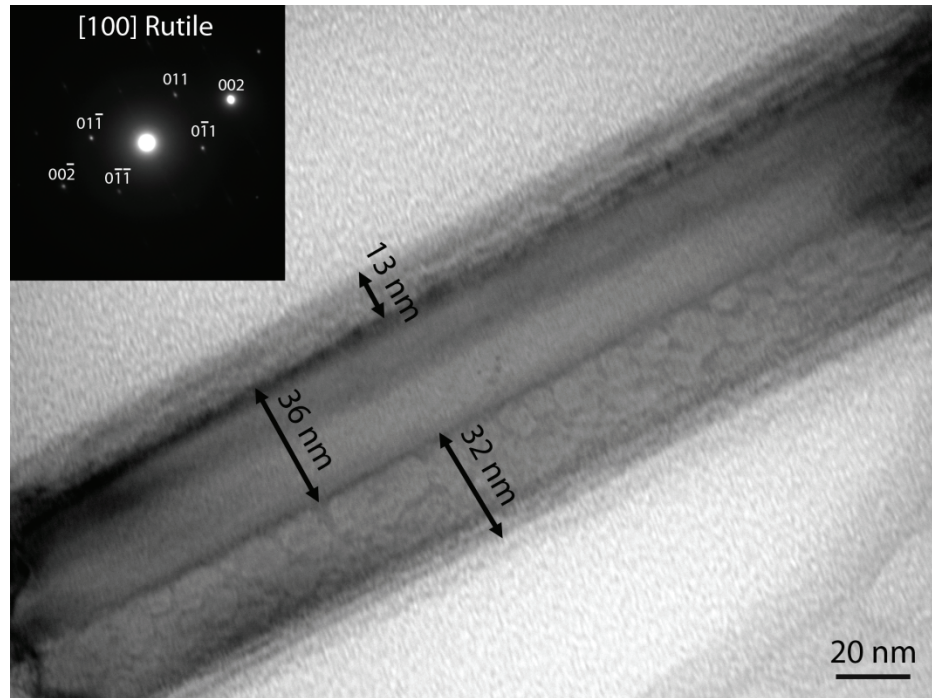
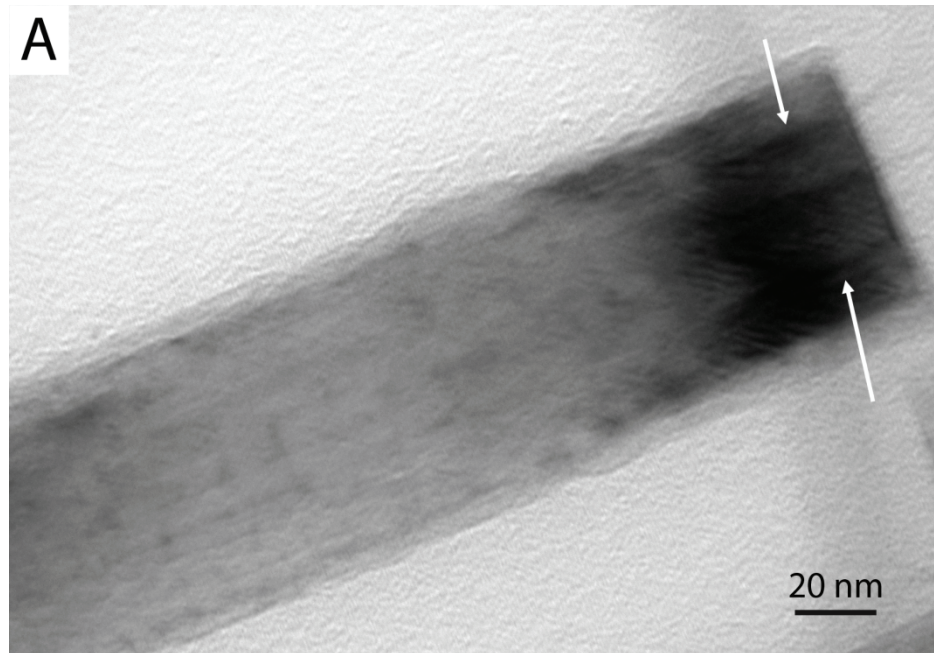


Figure 4.8: Higher magnification BF TEM image of NW exhibiting a core-shell structure. Corresponding SAD pattern shows a [100] zone axis.

Figure 4.9 B clearly shows 2 different crystal structures in the SAD pattern however, they appear to have a strong relationship to one another. This is indicated by the complete overlap of the $0\text{-}1\text{-}1\text{ g}$ of rutile and the $2\text{-}1\text{-}10\text{ g}$ of corundum. All other diffraction spot locations show two spots, each of which belonging to a different crystal structure, in close proximity to one another. The distance between these spots increases as you move further away from the $0\text{-}1\text{-}1\text{ g}$ of the rutile pattern as is observed in the comparison of the $0\text{-}11\text{ g}$ and $\text{-}1\text{-}120\text{ g}$ pair with the 002 g and $\text{-}3030\text{ g}$ pair.

Figure 4.10 is a BF TEM image of a single NW where the core is showing strong contrast while the shell displays almost no contrast at all. The SAD pattern for this wire can be indexed only to the rutile phase of TiO_2 . The high contrast of the core (dark in a

BF image) indicates that it is contributing to the diffraction pattern where as the absence of contrast from the shell indicates conditions are such that it is not diffracting strongly and as such is not contributing to the SAD pattern. However, further characterization employing DF imaging of this wire is required to confirm that the diffraction is only from the core. This would also confirm that the core is indeed rutile TiO_2 . If a similar analysis was performed under conditions such that the shell is diffracting and the core is not, one could determine conclusively the shell's crystal structure. The current results strongly indicate the core of the NW is the rutile phase TiO_2 and the shell is corundum (Al_2O_3) though further studies employing DF imaging in the TEM are required to confirm this. These should be completed once the instrument is operational again.



continued

Figure 4.9: A) Higher magnification BF TEM image of NW without a core-shell structure. B) Corresponding SAD pattern shows both a $[100]$ rutile and $[0001]$ corundum zone axes patterns.

Figure 4.9: continued

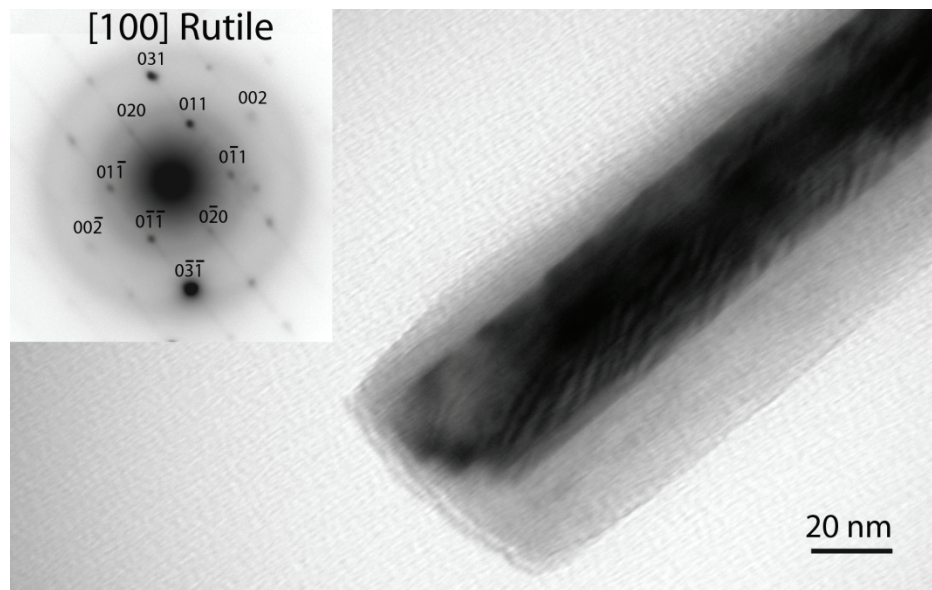
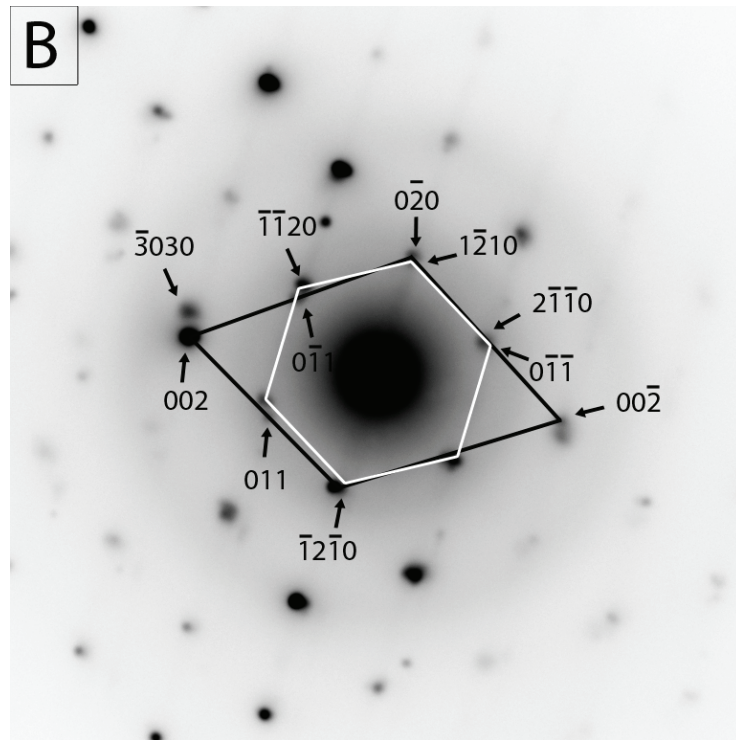


Figure 4.10: BF TEM image showing strong contrast from the core of the wire. SAD pattern shows only rutile TiO_2 with a [100] zone axis.

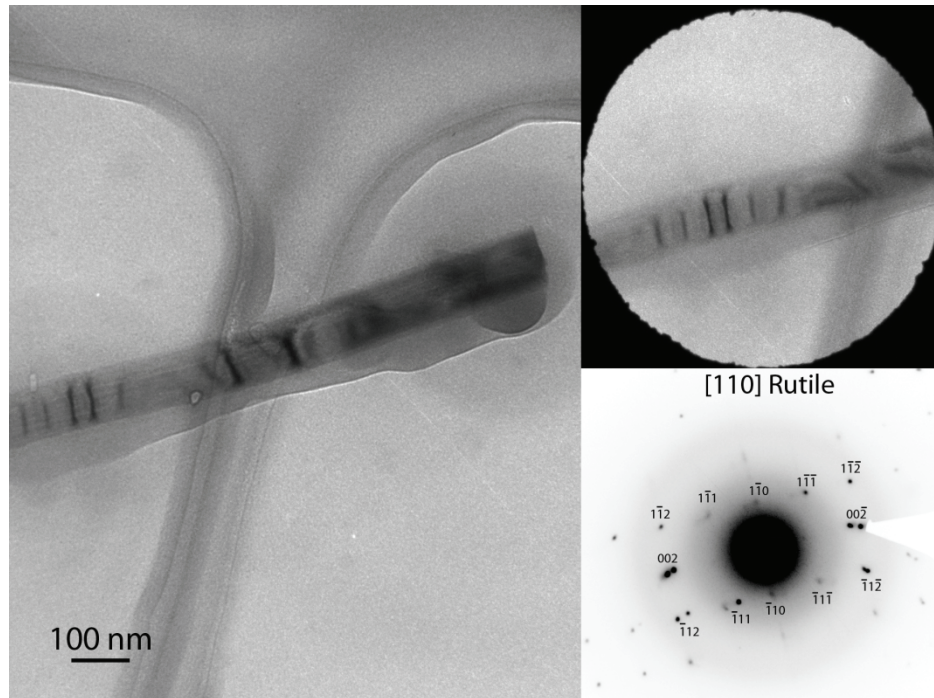


Figure 4.11: BF TEM image of a NW showing lines perpendicular to the NW's long axis. Corresponding SAD pattern shows a [110] zone axis rutile.

Figure 4.11 shows a BF TEM image of a single NW. Multiple lines were observed perpendicular to the growth direction of the NW. Double diffraction spots are clearly visible in the SAD pattern specifically in the 002 direction. Multiple diffraction spots in an SAD pattern are often due to twins or grain boundaries. To confirm this, dark field imaging of the NW was conducted using the 00-2 g vector as observed in **Figure 4.12**. The insets in **Figure 4.12** show the positioning of the objective aperture around the respective diffraction spots to compose the DF images. Two separate lines are clearly contrasting brightly against a dark background indicating they are strongly diffracting and contributing to the diffraction spot. These lines are a different orientation of rutile compared to the surrounding wire. This shows that the wire is not single crystal rutile

TiO₂ but rather is made up of alternating crystal orientations. This behavior has been observed in multiple NWs but is yet to be fully explored. Further analysis is required to better understand this behavior.

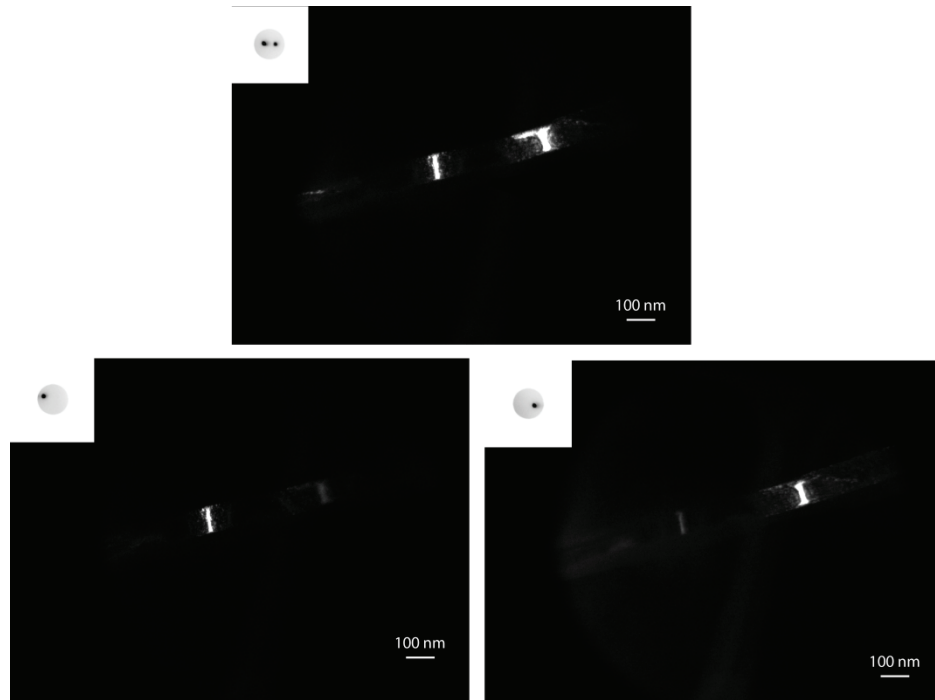


Figure 4.12: DF TEM images showing lines in NW to be a different orientation of rutile than the surrounding wire.

The previous discussion has been focused on the characterization of the NWs resulting from the oxidation of Ti64 in a low oxygen environment. SEM results show a dense coverage of NWs on the surface of the alloy samples after oxidation. The resulting NWs were less than 100 nm in diameter and several microns in length. The substrate microstructure prior to oxidation was found to have a direct impact on the resulting NW coverage due to the preference for NW growth on the β phase of titanium. XRD analysis

indicated the presence of both rutile TiO_2 and corundum (Al_2O_3). This was further confirmed by electron diffraction from a single NW (**Fig. 4.9 B**). BF TEM images with corresponding SAD patterns indicate a core-shell structure for the NWs where the core is rutile TiO_2 and the shell is corundum. However, this needs to be confirmed through the use of DF TEM imaging using low index \mathbf{g} vectors from each of the respective patterns. In this way, the area of the sample contributing to a specific \mathbf{g} from a selected diffraction pattern can be identified. The remainder of this chapter is focused on the discussion of the effects of oxygen concentration on growth and the application of the growth process to other substrate morphologies.

4.3.2 Effects of Oxygen Concentration on Nanowire Growth

In addition to temperature, the oxygen environment in which a metal is oxidized can have a profound impact on the resulting oxide. For example, Peng *et al.* thermally oxidized Ti metal substrates at 850 °C in three different oxygen environments: high purity oxygen, a low oxygen concentration Ar mixture (concentration not specified), and in acetone.[87] Both the low oxygen concentration mixture and the acetone heat treatments produced nanostructures but the high purity oxygen produced only a planar film. Due to its strong influence of $p\text{O}_2$ on the resulting oxide it was necessary to investigate the effect changing $p\text{O}_2$ would have on the resulting NWs. Previously, Ti alloy samples were oxidized in 4.8 grade Ar (99.998%) to produce NWs. One experiment had been conducted in which the oxygen concentration was increased to 1%. This experiment failed to yield NWs forming only an oxide scale instead.

To fully understand the impact of the oxygen concentration on the formation of TiO₂ NWs a detailed investigation of the growth of NWs under different oxygen environments was necessary. For this set of investigations the annealing temperature and duration remained constant and only the gas concentration was changed. The desired pO₂ was set in one of two ways: 1) A single gas cylinder containing the desired concentration of O₂ balanced with Ar was flown at 500 sccm or 2) a combination of two cylinders was used to set the desired pO₂ level. In the later, a cylinder containing 5000 ppm O₂ balanced with Ar was combined in the reaction chamber with a cylinder containing 4.8 grade Ar. The flow rates of the 2 gases were adjusted to obtain the desired oxygen concentration while maintaining an overall flow rate of 500 sccm. For example, to obtain a pO₂ of 19 ppm, the 5000 ppm O₂/Ar mixture was flown at 2 sccm while the balance of the 500 sccm total flow was made up by the Ar cylinder (498 sccm). The gas mixture was allowed to flow until the PO₂ was measured to be steady and constant in the reaction chamber before the furnace was ramped to 700°C at 23°C/minute. To facilitate in the equilibration of the oxygen concentration in the reaction chamber a cycle of 5%/95% H₂/Ar mixture flowing at 150 sccm for 1 minute followed by 20 minutes of the desired gas mixture at 500 sccm was performed three times. In this way a wide range of oxygen concentrations were tested to investigate the optimum pO₂ level for NW growth.

Figure 4.13 shows a typical pO₂ vs. time plot for a pO₂ experiment. One can see an initially fast decay of the pO₂ level gradually leveling out over time. The steps in the oxygen profile at early times are due to the cycling of H₂/Ar (5%/95%) with the desired O₂/Ar mixture (balanced for target pO₂) to enhance the rate of oxygen concentration

equilibration in the reaction chamber. The temperature profile has been plotted on the same graph to aid in the visualization of the experiment. The Temperature rises only after the pO_2 level has stabilized at the desired level. Initially, oxygen concentrations of 50%, 5000 ppm, 2000 ppm, 500 ppm, 250 ppm, 100 ppm, and 50 ppm were investigated. Several of the corresponding micrographs are shown in **Figure 4.14**. At high oxygen concentrations (50% - 500 ppm) only oxide scales formed and no NW formation was observed (**Fig. 4.14A**). The first observable occurrence of NW formation did not occur until 500 ppm. These wires were short in length and appeared to bundle together. As the PO_2 level was further decreased to 250 ppm the NWs no longer bundled but separated into individual, extremely short NWs (300 nm) with diameters of ~ 100 nm. At 50 ppm the average NW length increased to ~ 500 nm and the diameters decreased to approximately 50nm. At 20 ppm the average length increased to 1.2 μm while the diameters remained near 50nm (**Fig. 4.14D**).

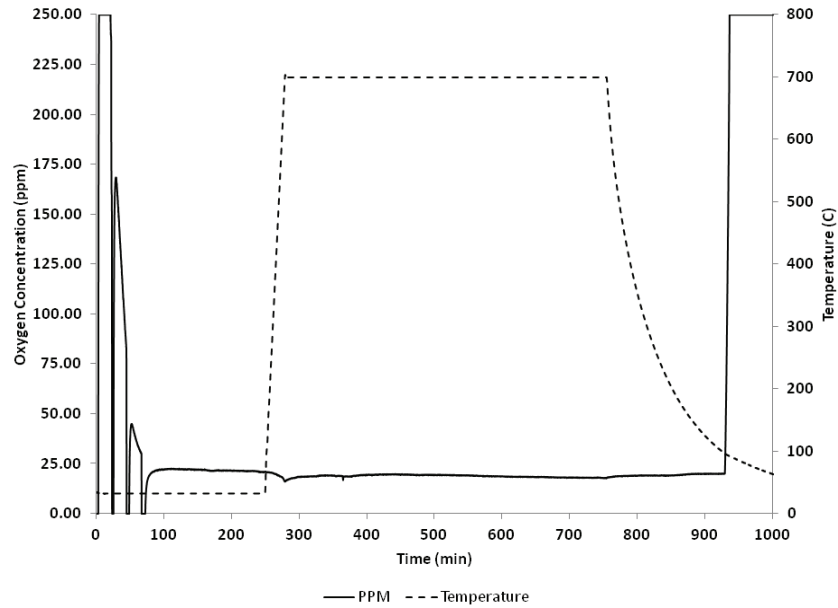
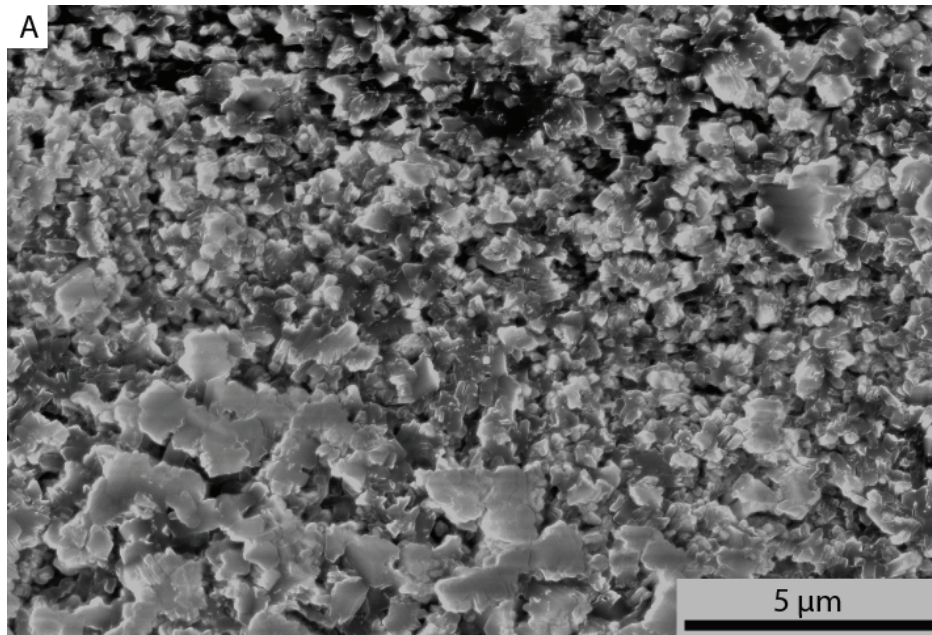


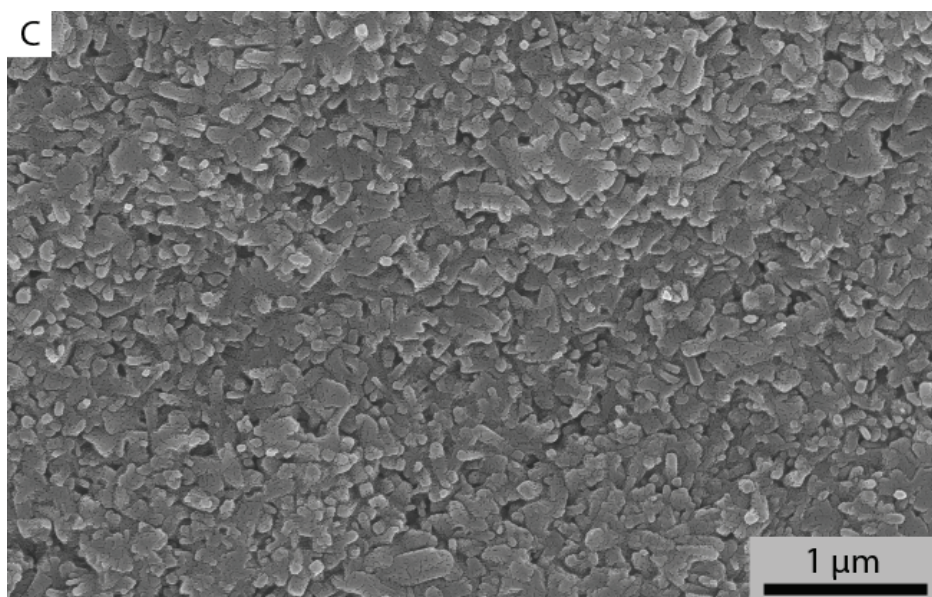
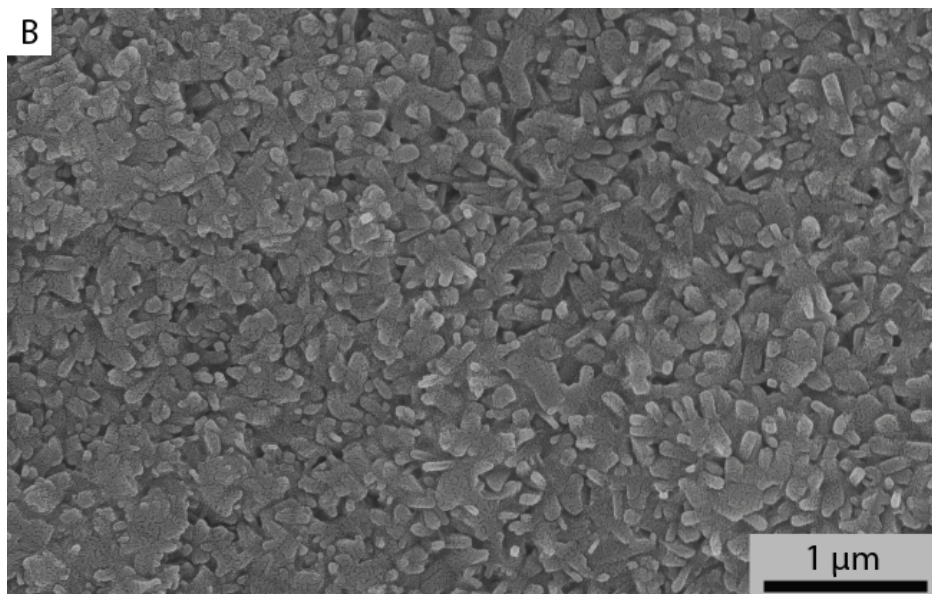
Figure 4.13: Plot of the oxygen concentration vs. time of a typical O₂ variation test. The temperature profile is plotted to aid in visualizing the experiment.



continued

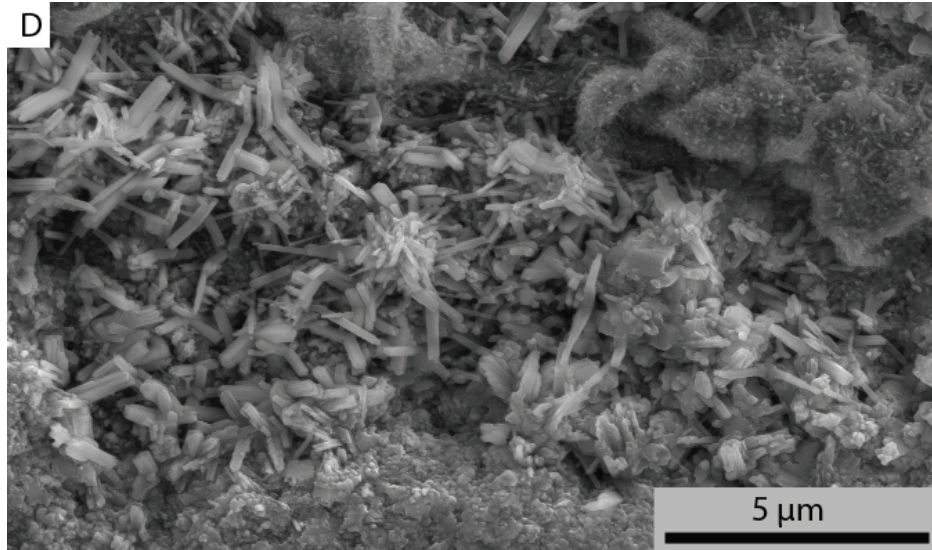
Figure 4.14: SEM micrographs of Ti64 oxidized at 700°C for 8 hours under 500sccm flow of A) 50%, B) 5000 ppm, C) 2000 ppm, and D) 500 ppm O₂ balanced with Ar.

Figure 4.14: continued



continued

Figure 4.14: continued



An experimental lower limit for control of the O₂ environment was reached at around 17 ppm due to the limitation of the lowest flow rate allowable by the digital flow meters. The next lowest step was flowing only 4.8 grade Ar which contains approximately 5 ppm of oxygen (measured and averaged over several cylinders). **Figure 4.15** shows an SEM micrograph of the surface of bulk Ti64 oxidized at 5 ppm O₂ (Ar only) for 8 hours at 700°C. Very few NWs grew on the surface of the alloy. Only small tufts of very short NWs can be seen. This is an indication of insufficient oxygen for NW Growth. Based on these results an O₂ concentration of 20 ppm was chosen as the optimum target PO₂ for further NW growth studies.

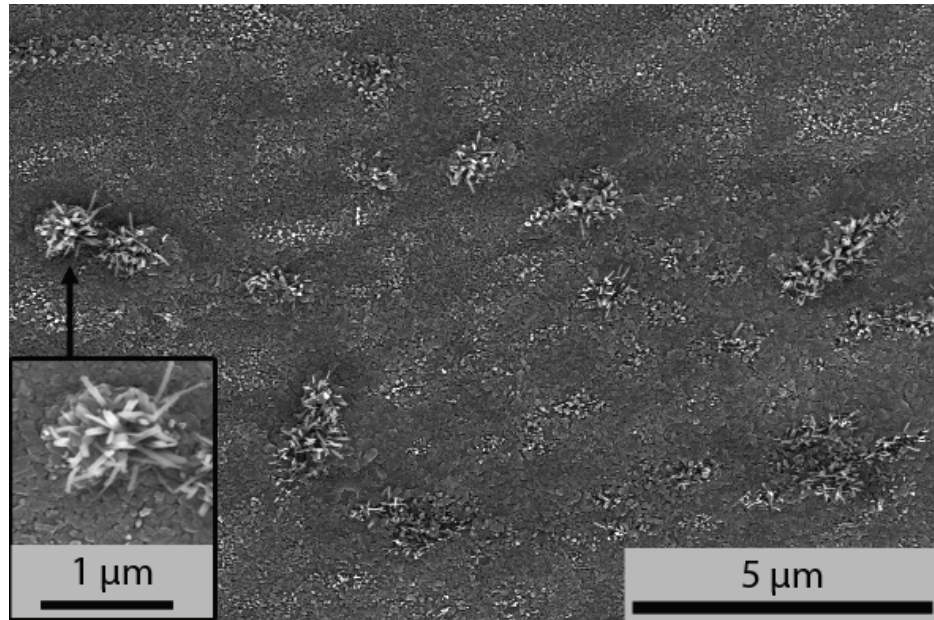


Figure 4.15: SEM micrograph of Ti64 bulk sample oxidized at 700°C for 8 hours in 5ppm of O₂.

The 4.8 grade Ar used in all of the previously described experiments is rated at 99.998% pure. This means any given cylinder of Ar can potentially contain up to 20 ppm (0.002%) of oxygen if we assume oxygen is the only impurity present. The actual oxygen concentration measured using a ZrO₂ sensor varied from 3-8 ppm from cylinder to cylinder. The oxygen environment during oxidation of the alloy samples to produce TiO₂ NWs varied as a function of time. Initially, the oxygen level was quite high being at or near atmospheric levels. As Ar gas was flown through the reaction chamber the excess O₂ was carried away reducing the oxygen environment. **Figure 4.13** shows this decaying pO₂ behavior. For all but the oxygen concentration studies the furnace ramp was started simultaneously with the introduction of Ar into the gas chamber. This resulted in a constantly changing oxygen environment during the ramp and early temperature hold

period of the oxidation process. The decreasing O_2 environment typically produces longer NWs ($\sim 3 \mu\text{m}$) with a tapering diameter, as can be seen in **Figure 4.16**, compared to the 20 ppm sample where NWs of slightly more than $1 \mu\text{m}$ in length were observed. This indicates that a high pO_2 level during the early stages of oxidation may be desirable to increase the NW coverage and length. This effect and the optimization of the high pO_2 decreasing to a low pO_2 during early oxidation have not been investigated.

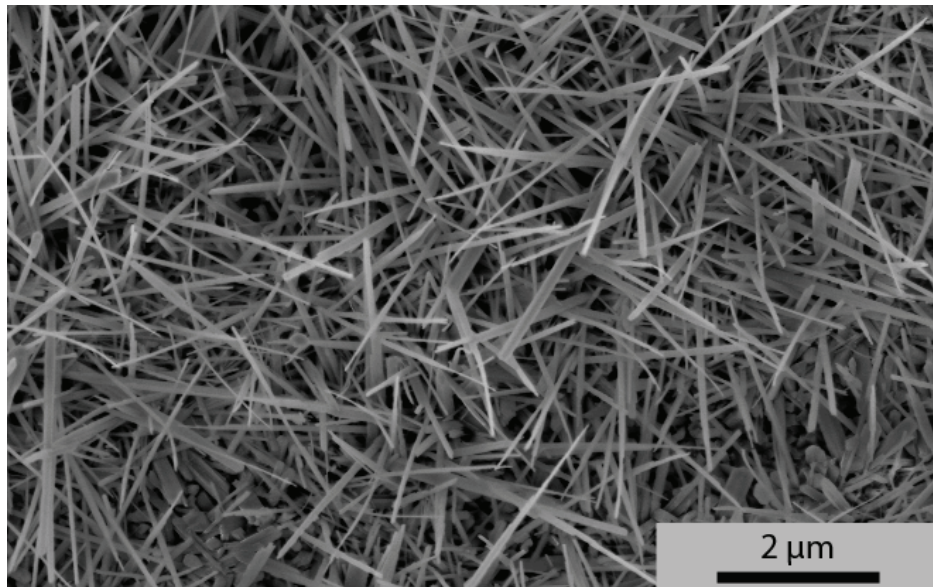


Figure 4.16: SEM micrograph of tapered NWs grown by oxidation at 700°C for 8 hours starting at ambient O_2 concentration decreasing to 5ppm during the anneal.

4.3.3 Application of Growth Process to Various Substrate

Configurations

To extend the range of possible applications for this technology other substrate geometries were investigated. All of the previous discussion and experiments were

focused on bulk Ti alloy substrates typically cut from larger pieces. The oxidation process was also applied to Ti64 foil, both Ti64 and Ti5-5-5 powders, and Ti5-5-5 thin film deposited by DC magnetron sputtering. The following discussion briefly outlines some results of these investigations.

Ti5-5-5 particles produced in house by atomization were oxidized at 700°C for 8 hours under 500 sccm of flowing Ar to produce TiO₂ NWs. The furnace ramp and the gas flow were started at the same time. **Figure 4.17** is an SEM micrograph showing the typical surface morphology of the Ti5-5-5 particles oxidized by this process. The atomization process used to produce the Ti particles resulted in a range of particle sizes. The particles were sorted by size using subsequently smaller mesh sizes resulting in five particle sizes: 1) greater than 180 μm (+80 mesh), 2) between 180 μm and 125 μm (+120 mesh), 3) between 125 μm and 75 μm (+200 mesh), 4) between 75 μm and 45 μm (+325 mesh) and 5) smaller than 45 μm. The impact of oxidation temperature and duration were systematically investigated in a manner consistent with the previously described approach with almost identical results. At low temperatures, 600°C (**Fig. 4.18A**), no NWs formed and at relatively high temperatures, 800°C (**Fig. 4.18C**) and 900°C (**Fig. 4.18D**), only short NWs and large faceted crystals formed, respectively. The optimum growth temperature was found to be consistent with that of the bulk material, 700°C (**Fig. 4.18B**). Also, an increase in the annealing duration resulted in an increase in the average length of the NWs as can be seen by comparing **Figures 19 A and B**. The effect of particle size was also investigated and found to be negligible. Theoretically, there should be a lower limit to the particle size at which NWs would still be able to form

corresponding to the thickness of the oxide layer formed prior to NW growth. That is, if the particle size is reduced to a size that is roughly twice the size of the initially formed oxide layer, there would be insufficient titanium after the initial oxide layer formed to produce NWs. However, all particle sizes tested produced NWs and thus are above this limit.

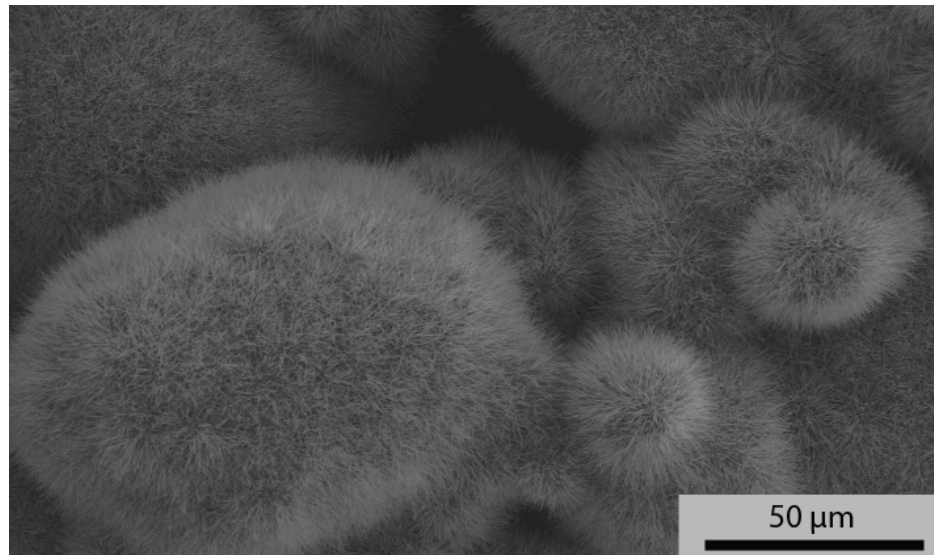
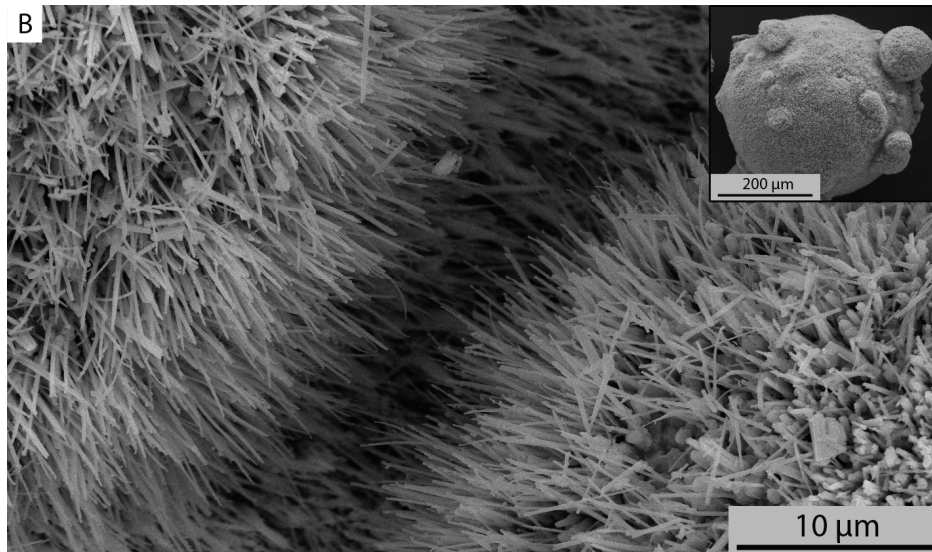
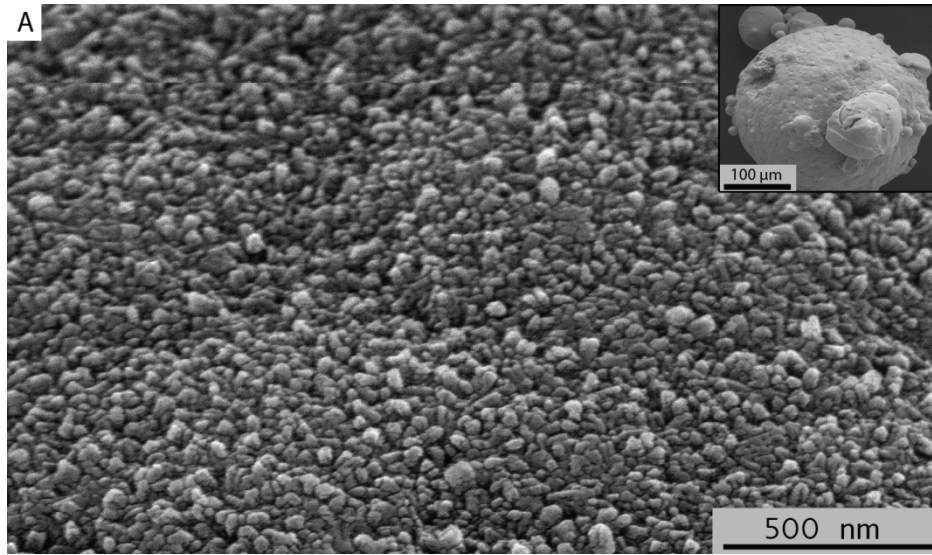


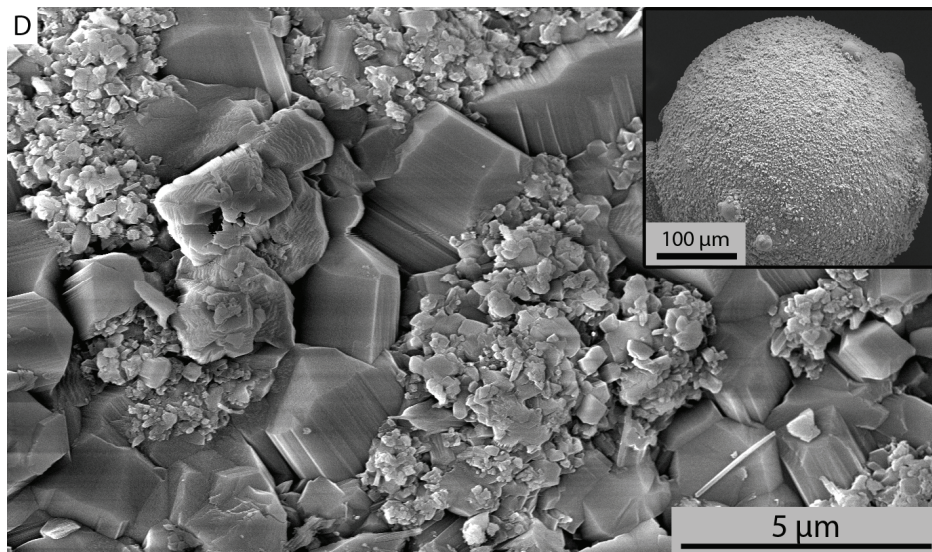
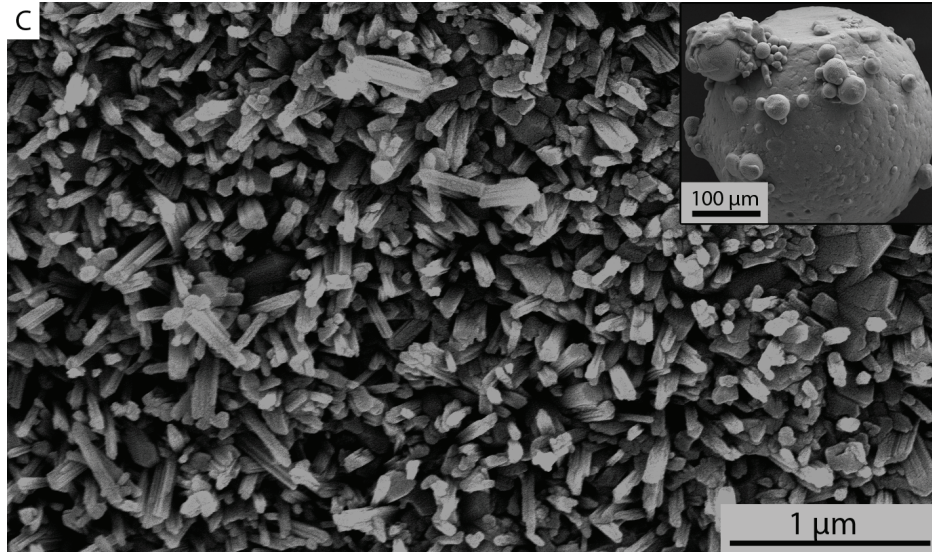
Figure 4.17: SEM micrograph of Ti5-5-5 particles oxidized at 700°C for 8 hours under 500sccm flowing Ar.



continued

Figure 4.18: SEM micrographs of Ti5-5-5 particles oxidized for 8 hours under 500scm flowing Ar at A) 600°C, B) 700°C, C) 800°C, and D) 900°C. Insets show low magnification image of particle oxidized.

Figure 4.18: Continued



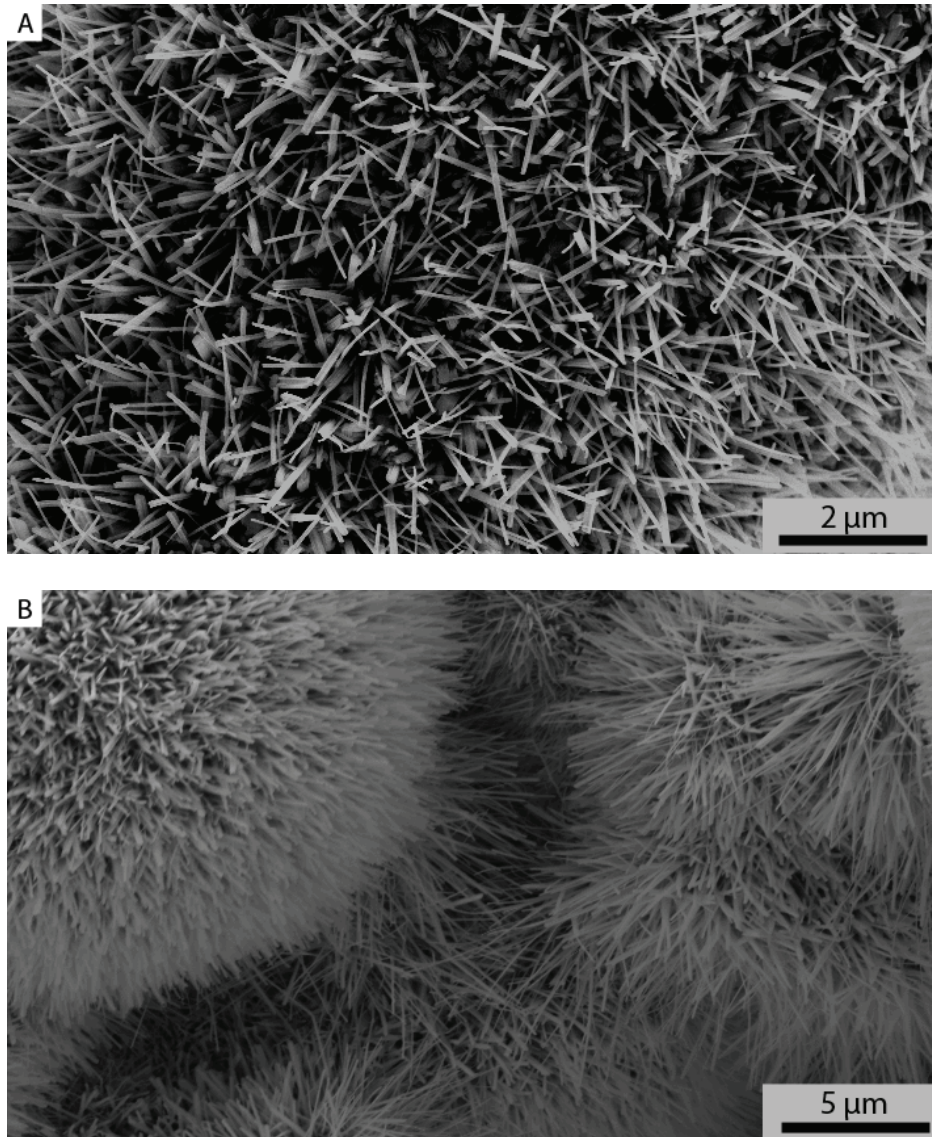
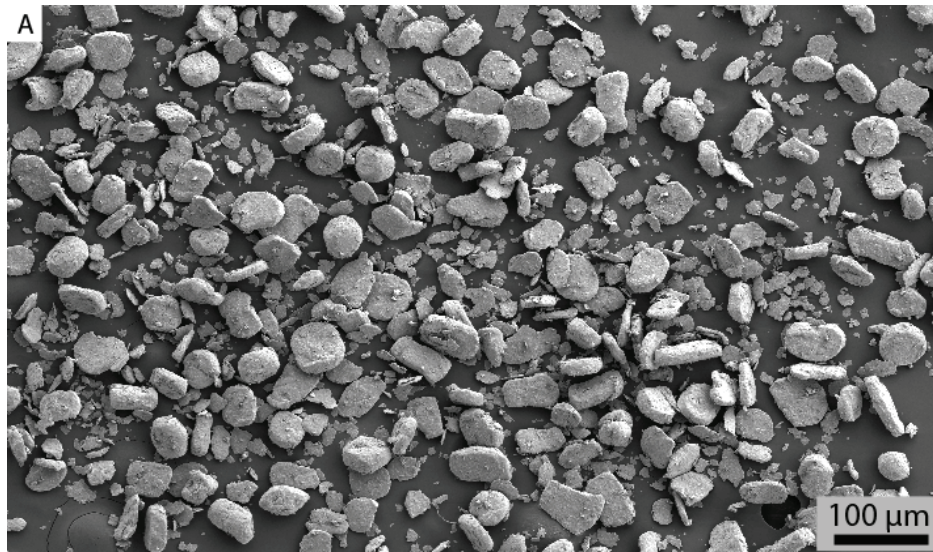


Figure 4.19: SEM images of Ti5-5-5 particles oxidized at 700°C under 500scm of flowing Ar for A) 6 hours and B) 16 hours.

To investigate the viability of using this NW growth technique on a commercially available Ti alloy powder, Ti64 powder was purchased and oxidized to produce NWs. The Ti64 powder was not produced by atomization but rather by mechanical milling as a result, the particles were not spherical in shape. The particles had an average diameter of

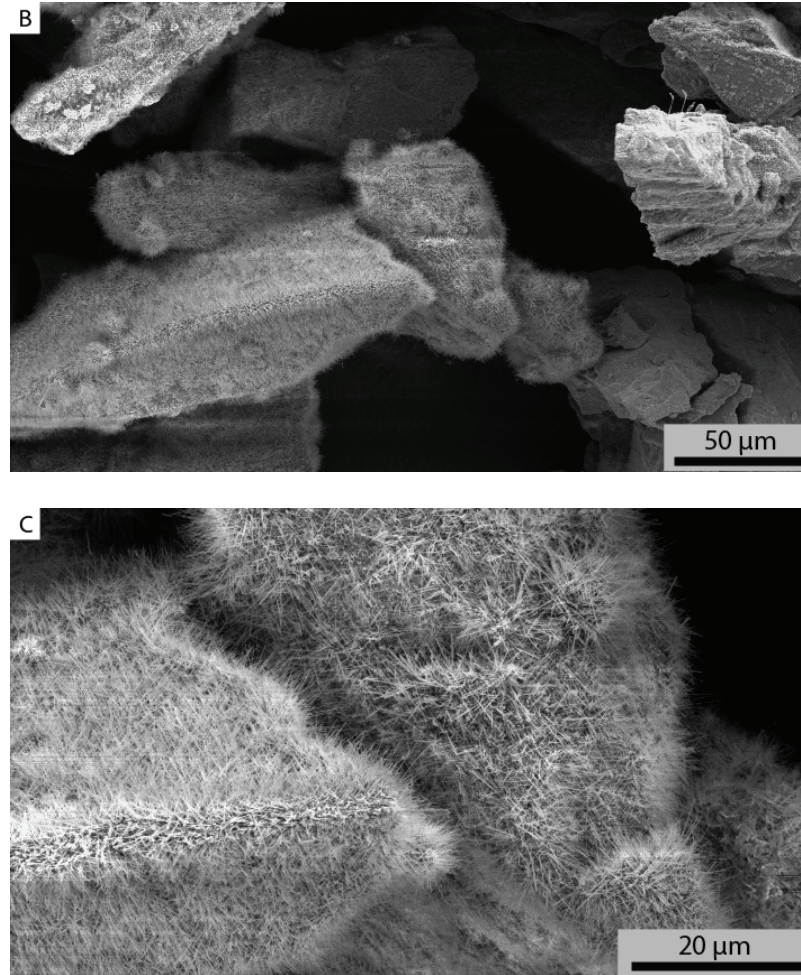
300 μm as received. The particles were ball milled to reduce the particle size down to 100 μm as shown in **Figure 4.120A**. One should be able to further reduce the particle size by increasing the ball milling time however this has not yet been optimized. The standard oxidation process was extremely successful in producing NWs on the Ti64 alloy particles (**Fig. 4.20B-C**).



continued

Figure 4.20: SEM images of A) Ti64 particles after ball milling to reduce average particle size, B) low magnification, and C) higher magnification of as-received Ti64 particles after oxidation at 700C for 8 hours under 500sccm flowing Ar.

Figure 4.20: Continued



The application of the NW growth process to thin films is attractive for a number of reasons. It would enable one to coat an existing non-Ti material or device with a Ti thin film and oxidize it to produce NWs. It would also allow for the selective application of this process to only a specific area or region of a device where semiconducting NWs are desired. There are no commercially available α - β or β -stabilized Ti alloy sputtering targets. As such, one was manufactured in house using Ti5-5-5. A large piece of Ti5-5-5

was machined to a 3” diameter disc 0.25” thick. The target was polished and vacuum annealed to remove residual stresses from the machining process. Using this target, Ti alloy thin films were deposited via DC magnetron sputtering. Various power (60-180 W), pressure (4-5.5 mTorr), and duration (0.5-6 hours) combinations were explored. The resulting thin films were characterized by SEM, XRD and pump-probe optical time-domain thermo reflectance (TDTR). They were then oxidized under a 500 sccm flow of 20 ppm O₂ balanced with Ar for 8 hours at a temperature of 700°C. The resulting NWs are shown in **Figure 4.21**.

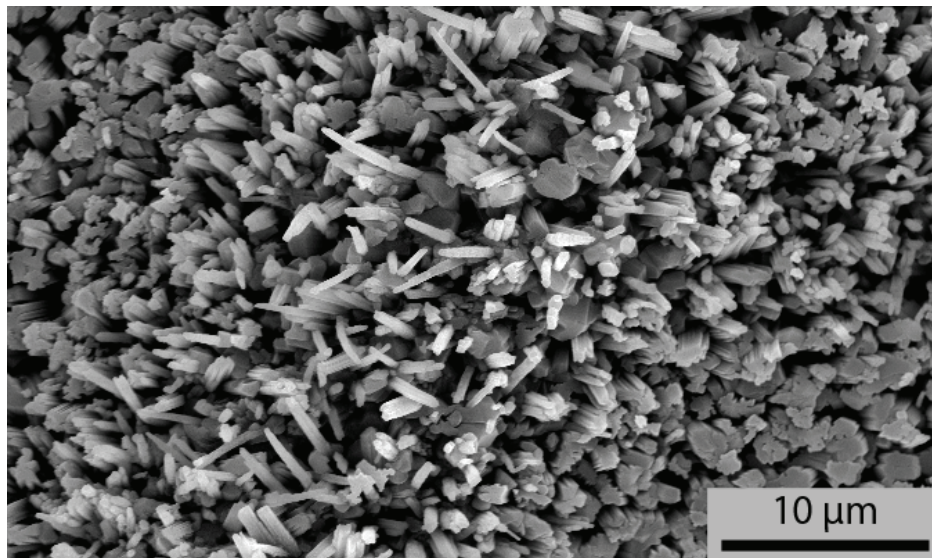


Figure 4.21: 1 μm thick β thin film oxidized at 700°C. for 8 hours in 20 ppm of oxygen

4.4 Conclusions

The growth process for producing TiO₂ NWs on a variety of Ti alloy substrates by thermal oxidation was previously studied by Lee.[175] The effect of oxidation

temperature, duration, gas flow rate, and Ti alloy composition were investigated. Of these processing conditions annealing temperature and alloy compositions were found to have the greatest impact on the resulting NW morphology. At temperatures below 600°C or above 800°C NW growth was not observed. Only α - β or β -stabilized Ti alloys containing aluminum produced NWs under the growth conditions explored. The flow rate at which the oxidizing gas was flown had little effect on NW growth. The duration of the oxidation only had an impact on the overall length of the NWs. The present work carried out an extensive study to investigate the effects of oxygen concentration during the oxidation process on the resulting NWs. It was found that at constant oxygen concentrations above 250 ppm NW growth did not occur.

The optimum growth conditions that produced NWs on the Ti alloy samples can be summarized as follows: a high initial oxygen concentration at the start of the furnace ramp (*e.g.* 20% O₂) followed by a very low oxygen concentration (*e.g.* 20 ppm) for the remainder of the anneal, an annealing temperature of 700°C, an Ar flow rate of 500 sccm, for a total oxidation duration of approximately 8 hours. Using these conditions NWs were successfully grown on a number of Ti alloys. This process was successfully transferred to a variety of titanium alloy substrate configurations including bulk metal, powders, foils, and thin film.

Recent efforts to advance the characterization of the nanostructures formed on titanium alloy substrates in an oxygen deficient environment have shown the NWs to be core-shell in structure. Initial diffraction data indicate the core is rutile TiO₂, the shell may be corundum (Al₂O₃), and the NWs' long axis is parallel to <002> rutile. However, further

investigations involving the use of dark field TEM imaging are required to confirm the interpretation of the diffraction data.

This process has been shown to work on a variety of substrates by experimental means however a deeper understanding of the mechanisms governing the growth of the NWs is desirable for wide application of this process. Lee, the pioneer of this method made some progress in the understanding of the growth mechanism but left some issues unresolved.

Table 4.1 gives a listing of the oxidation parameters investigated by Lee and the recent contributions by the author for the purpose of clarity. The following chapter attempts to build on his base of understanding by utilizing the new characterization information combined with experimental evidence to further the mechanism used to explain the growth of NWs on titanium alloys under a limited supply of oxygen.

Researcher	Contributions to Process Characterization				
Lee [174]	Temperature	Duration	Flow Rate	Alloying Elements	Substrate Microstructure
Key Findings	<ul style="list-style-type: none"> • Low T (~600°C) = Oxide Scale • 700°C = NW Growth • 800°C = NW + Faceted Crystals • High T (>900°C) = Faceted Crystals 	Longer Oxidation = Longer NWs	Little Effect on NW Growth	<ul style="list-style-type: none"> • Al Improved NW Yield • Mo & V had no observed effect 	Preference for NW growth on β phase shown through alloy variation
Current Study	Oxygen Concentration	Substrate Morphology	TEM Characterization	Phase Identification	Substrate Microstructure
Key Findings	<ul style="list-style-type: none"> • No NW growth > 500 ppm • NW Growth Improved with decreasing pO_2 • Best NW yield in high initial pO_2 decaying over time 	Process successfully applied to Ti: Particles, Foils, Bulk metal, and Thin Film	<ul style="list-style-type: none"> • NWs are core-shell in structure • Growth direction is $\langle 002 \rangle$ in rutile 	<ul style="list-style-type: none"> • Both corundum and rutile TiO_2 were observed • Core appears to be rutile • Shell may be corundum 	Preference for NW on β phase confirmed by varying microstructure of Ti64 via heat treatment

Table 4.1: Contributions of respective researchers to the understanding of oxidation parameters for NW growth and the characterization of the resulting NWs.

Chapter 5: Mechanism of Formation for TiO₂ NWs on Ti Alloy Substrates

5.1 Introduction

The production of core-shell structured nanowires (NWs) by oxidation of titanium alloy samples in a limited oxygen environment has been presented in the previous chapter. This work was pioneered by Lee and presented in his doctoral thesis.[175] A detailed investigation of the parameters governing the formation of the NWs on the alloy surfaces was presented. Recent work has attempted to expand upon Lee's investigation as presented in the previous chapter and to provide new insight into the growth of NWs on alloy substrates with recent experimental results. In his thesis, Lee also proposed a theory of growth to explain the formation of NWs on the alloy substrates. His theory was based on three main questions: *i) are there any catalyst present in the system which promote anisotropic growth, ii) does the nanowire growth occur via the supply of source material as a gas phase or through solid state diffusion, and iii) where does the growth the of nanowires occur; at the tip of the nanowire or the base?*[175]

The following section is a brief description of Lee's findings and answers to these questions. This is followed by a description of the mechanism proposed by Lee. The final portion of this chapter poses additional questions not postulated by Lee which may aid in further understanding the mechanism(s) promoting the formation of one dimensional (1-

D) nanostructures by this oxidation process. Finally, experimental evidence is presented to answer some of the proposed question and a more complete mechanism is presented to explain the formation of NWs on titanium alloy substrates by oxidation in a limited supply of oxygen.

5.2 Previous Work

The first question proposed by Lee dealt with the confinement of oxide growth to 1-D.[175] The confinement of growth to 1-D for NW production can be obtained by either physical means as is the case in template assisted growth.[25, 178] However, it could also be provided by preferential adsorption of the source material at chemically active sites such as catalyst locations as in the vapor-liquid-solid (VLS) growth method, or atomic steps formed by screw dislocation intersecting the surface in the VS mechanism. The template assisted confinement method was ruled out as a possible means of confinement as no porous template was intentionally used in the formation of NWs on Ti alloy substrates. However, the role of chemically active sites in providing confinement of growth to 1-D could not be so easily dismissed. The role of catalyst elements in the confinement of nanostructured growth to 1-D was discussed extensively in Chapter 2. Briefly, liquid droplets are formed by an eutectic alloy reaction between a source material and a metal catalyst. The classical example is that of a silicon substrate and gold nanoparticles.[49] The droplet, having some solubility of the source material, acts as a preferential deposition site for adsorbing the source material from the gas phase. The adsorbed material diffuses through the liquid droplet to the droplet-substrate interface where it solidifies forming the nucleation point for a 1-D structure. The catalyst droplet

remains at the tip of the growing NW throughout the growth process. A metallic cap is commonly present at the tip of the NW after the process and has been considered the identifying characteristic of the VLS growth process. That is, if a cap is observed at the tip of NWs after a growth processes has completed it is assumed the process proceeded by the VLS mechanism. Therefore, it was prudent to examine the NWs resulting from the oxidation of titanium alloys to look for a metallic cap. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis combined with chemical analysis by electron dispersive spectroscopy (EDS) showed no metallic cap present at the tip of the NWs.[175]

These results were conclusive for the short wires grown on commercially pure titanium sample as only titanium and oxygen were identified in the NWs after oxidation.

However, aluminum in addition to titanium and oxygen was identified in the NWs resulting from the oxidation of Ti-5-5-5 samples. Based on thermodynamic data it was concluded that no liquid phase was stable in the titanium-aluminum-oxygen system at the oxidation temperature. Additionally, the other alloying elements in the system, iron, molybdenum, and vanadium, were eliminated as liquid catalyst candidates based on thermodynamic data. Thus, it was concluded to be very unlikely that the growth of the NWs on alloy samples was the result of the VLS mechanism.

With the elimination of the VLS mechanism as the means of confining growth to one dimension in the titanium alloy system attention was turned to investigating the possibilities of growth by vapor-solid (VS) interaction or by metal oxidation via bulk diffusion. Both of these processes for NW growth were discussed in detail in Chapter 2.

Briefly, vapor-solid growth involves the deposition of a vaporized source material. The vapor is often formed by thermal evaporation [179], laser ablation [180], or carbothermal evaporation [45] techniques. In contrast, growth by oxidation involves only oxygen in the gas phase. To establish the possibility of growth by the VS method Dr. Lee investigated the likelihood of the presence of vaporized titanium in sufficient quantities as to account for the NW growth observed on the alloy substrates. Two sources of vaporized titanium were considered: *i) direct vaporization of Ti from the substrate* and *ii) vaporization of a volatile oxide phase after the formation of an initial oxide layer*.

The vapor pressure of titanium was found to be 1.34×10^{-15} torr at 973 K (700°C). Using the typical growth parameters and sample surface area of 8 hours at 700°C and 0.25×10^{-6} m², respectively, the number of Ti molecules impinging the surface of the sample during a growth treatment would be 1.6×10^7 molecules.[175] It was then assumed that all impinging gas molecules are converted to TiO₂ by the following reactions



producing a total of 2.68×10^{-17} moles of TiO₂(s). The possible weight gain of the sample was then calculated to be 2.14×10^{-15} g. The actual weight gain of the sample during NW growth was measured to be 0.037g by thermal gravimetric analysis (TGA). Thus, it was concluded that insufficient titanium was present in the vapor phase to account for the growth of NWs.

There have been reports of NW growth by the VS mechanism where a volatile intermediate oxide species supplied sufficient vapor pressure of the source material to allow for growth by the VS mechanism.[16] This information led to an investigation of possible early forming oxides that could be capable of producing sufficient vapor pressure of titanium to account for the large weight gain of the sample. Titanium oxides including TiO, TiO₂, and Ti₂O₃ were investigated. All three oxides had lower vapor pressures at the processing temperature than that of titanium metal. Thus, it was concluded that NW growth could not have occurred by the VS mechanism due to an insufficient source of vaporized titanium.

Based on the previously described analysis the growth of NWs on titanium substrates was concluded to be caused by the oxidation route. However, one of Lee's questions still remained; *does growth occur at the tip or base of the NW?* To investigate this, a set of experiments was conducted in which oxidation of titanium alloy samples was performed with a change of temperature during the oxidation process. The basis for this approach is the concept that the reaction rate between titanium and oxygen is a function of the oxidation temperature. An increase in the temperature would result in an increase in the reaction rate whereas a decrease in temperature would slow the reaction. Two different heat treatments were used in this investigation. The first oxidized the sample at 700°C for 8 hours after which the temperature was increased to 800°C and held for an additional 4 hours. The NWs were found to maintain their shape after the 800°C treatment even though this temperature previously produced only large faceted crystals. Additionally, a change in the diameter of the NWs was observed at the tip of the NW compared to the

trunk. **Figure 5.1 A** shows a previously unpublished image of the NWs resulting from this 2-step heat treatment process. The body or trunk of the NW is of uniform diameter. A sharp increase in the NW diameter is observed near the tip. This change in diameter was attributed to the increase in the reaction kinetics between oxygen and titanium at the increased temperature of 800°C. This experiment was used as evidence of growth occurring at the tip of the NWs. It was postulated that if growth occurred at the base, a thickening of the NW would have been observed near the NW substrate interface. However, this experiment alone was not sufficient to completely rule out growth from that base. An additional experiment was conducted using a 3-step heat treatment process where the first two steps were identical to those used to produce **Figure 5.1A**. The additional third step consisted of a reduction of temperature down to 600°C, a temperature that had previously not produced NW growth. The resulting structure is shown in **Figure 5.1 B**. In this image, three different NW diameters are observed, the smallest of which is at the tip of the NW. The decrease in NW diameter was attributed to the 600°C oxidation step. Since it occurred at the tip of the NW, it was concluded that growth must be occurring at this point. Additionally, these experimental results lead. Lee to the conclusion that growth of the NWs was due to diffusion of titanium and that titanium must always be available at the tip of the NW.[175]

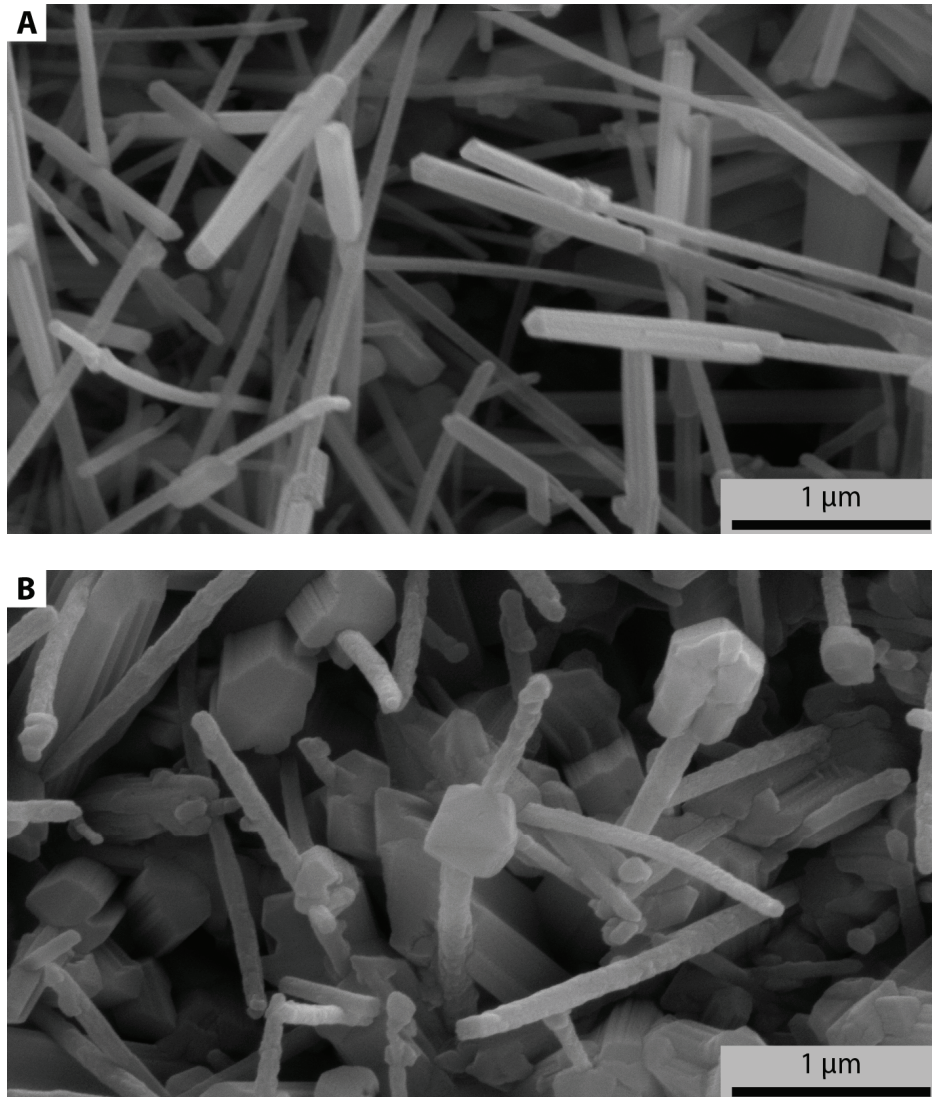


Figure 5.1: SEM images of Dr. Lee’s A) 2-step and B) 3-step oxidation investigations to determine if NW growth occurs from the tip or the base of the NWs.

Finally, a description of the growth process for producing NWs on titanium alloy substrates was presented broken down into four distinct stages. This description was based on SEM observations of samples oxidized for a variety of times (0.2, 0.5, 0.8, 1, 1.5, 3, and 6 hours). The four stages of growth were presented as follows: 1) formation of

a cracked planar oxide scale, 2) the formation of individual nanosized islands of TiO₂, 3) individual islands grow into NWs, and 4) the length and density of the NWs increase until full coverage of the sample is obtained.

Convincing arguments were made for the mechanism of growth being related to the oxidation of the alloy substrates rather than by the VLS and VS mechanisms.

Additionally, it was shown that growth occurred at the tip of the NWs rather than the base. This supports the argument that diffusion of Titanium from the bulk metal up to the tip of the NWs is required for NW growth to occur. However, several facets of this growth process remain unexplained and as such are missing pieces in the previously presented growth mechanism. The remaining gaps in understanding can be summarized by the following questions: i) *What causes the transition between stages 1 and 2 during NW formation*, ii) *What occurs during oxide formation that promotes transition to 1-D*, and iii) *Why is growth inhibited on the sides of the NWs?* The remainder of this chapter is focused on the experimental exploration conducted in an attempt to find answers to these questions.

5.3 Experimental

Ti64 (grade 5, Ti-6 wt % Al- 4 wt % V; Onlinemetals, Seattle, WA) were used for the Ti oxidation experiments. Bulk samples were cut using a diamond cutter (LECO, part number 801-136) and mechanically polished using SiC sand paper (1200 grit). After polishing, all samples were cleaned by the following procedure including a rinse in deionized (DI) water between each step: 1) 5 minute ultrasonication in acetone, 2) 5 min ultrasonication in methanol, and 3) 5 min ultrasonication in DI water. The samples were

inserted into a quartz tube (OSU Glass Shop) which was then placed in a horizontal tube furnace (Lindberg, TF55035A) for gas heat treatments. The oxidation environment was set by flowing the desired gas or gas mixture at a target flow rate maintained by a digital gas flow meter(s) (C100L, Sierra) while the oxygen partial pressure in the gas was monitored by an oxygen sensor (ZRO2000, Alpha Omega Instruments) at the output end of the reaction chamber. The furnace temperature and gas flow rate were computer controlled through an instrument control and data acquisition LabView program written in-house. The oxygen concentration was converted to a current by the oxygen sensor, monitored by a data acquisition system (34972A, Agilent) and read into the LabView program for collection and display. Samples were air quenched at the desired time by opening the furnace to air and removing the quartz tube from the furnace hot zone. The quartz tube remained sealed and the gas mixture flow through the chamber was maintained.

After quenching, SEM (FEG-SEM, Model Sirion, FEI, Oregon) was used for high resolution observation to detect changes in the surface morphology of the specimens at sub-micron scales. Crystal structure verification was performed using XRD analysis (Bruker XD). Cross-sectional samples were then prepared in a Dual Beam scanning electron microscope (SEM) and focused ion beam (FIB) (FEI, Helios 600). Prior to cross-sectioning, samples were coated with a layer of Au using a sputter coater (Model 3 Sputter Coater 91000, PELCO) at a plasma current of ~ 15 mA for 7 min. The structure of the resulting cross-sectional foils was examined with a transmission electron microscope

TEM (HRTEM, Model TF20) in high angle annular dark field HAADF imaging mode and elemental analysis was performed by energy dispersive spectroscopy (EDS).

5.4 Results

To investigate what causes the transition from the planar growth of a continuous oxide to the highly anisotropic 1-D growth observed cross-sectional samples at various points in the oxidation process were prepared and analyzed by SEM, XRD, TEM and EDS analysis techniques.

5.4.1 Determination of Quenching Times

The oxygen consumption during oxidation was used to determine at which times to quench the sample. **Figure 5.2** shows a typical oxygen and temperature profile for an oxidation experiment. A drastic decrease in the oxygen concentration is observed at very early times in the oxidation process, approximately when the furnace reaches a temperature of 700°C. The oxygen concentration continues to fall until a minimum is achieved at approximately 20 min of oxidation at 700°C. The concentration then recovers steeply and after an additional 20 min a plateau is reached. The oxygen concentration then remains constant for the duration of the oxidation process at approximately 2 ppm below the starting concentration. This behavior was observed in almost every sample oxidized at a constant oxygen concentration. To see if the drop in oxygen concentration upon heating was an effect of the gas equilibration at the oxidizing temperature a test was conducted without a titanium sample in the reaction chamber. No change in oxygen concentration was observed throughout the test. Thus, it was concluded that the change in oxygen concentration was due to the oxidation of the titanium alloy.

Based on the profile in **Figure 5.2**, three points in the oxidation time were chosen for quenching experiments; 20 min, 45 min, and 390 min after the furnace reached 700°C. These oxidation times corresponded to the lowest point in the oxygen concentration, just after the concentration recovered, and well into the oxidation process after significant NW growth; points 1, 2, and 3 respectively in **Figure 5.2**. By analyzing the oxidation process at these points the formation of the oxide layer could be observed and the initiation of NW growth from a planar oxide could be explained.

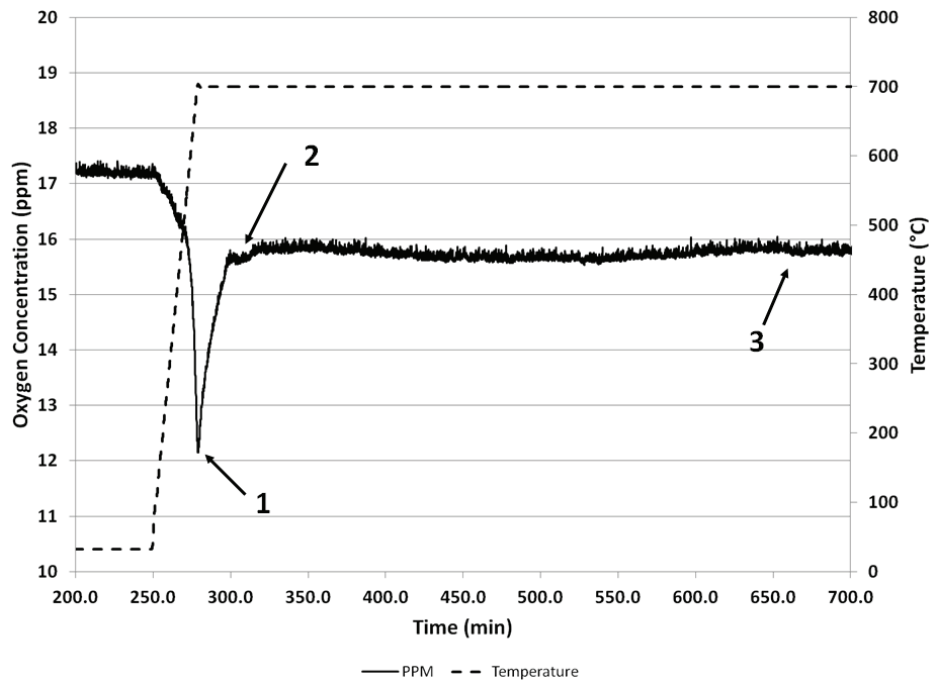


Figure 5.2: Plot of oxygen concentration vs. oxidation time used to select three different oxidation durations from which to make cross-sectional foils. The numbers 1, 2 and 3 on the plot correspond to the points at which samples were quenched.

5.4.2 Sample Characterization

5.4.2.1 SEM Characterization of Surface Morphology

All samples' surface morphologies were characterized by SEM prior to coating with Au.

Figure 5.3 shows an SEM micrograph of the surface of the sample quenched after 20 min of oxidation at 700°C in 17 ppm of oxygen. Individual islands are clearly visible on the surface of the sample. This sample was quenched at the bottom of the dip in the oxygen concentration profile in **Figure 5.2**. The surface morphology of the sample quenched after 45 min, after the oxidation profile plateau, is shown in **Figure 5.4**. Short NWs are already present on the surface of the sample. The final quench sample oxidized for 390 minutes was covered in NWs as can be observed in **Figure 5.5**. Comparing the surface morphologies of the 3 quenched samples an increase in the length and density of the nanostructured growth is clearly visible. Additionally, a transition growth between nanoislands and NWs is observed between the two earliest quench samples. Oxidation past 45 minutes only showed an increase in NW length and density as observed by comparing **Figure 5.4** and **Figure 5.5**. These three samples appeared to be excellent candidates for cross-sectional investigation of the oxide formation at various stages in the NW growth process.

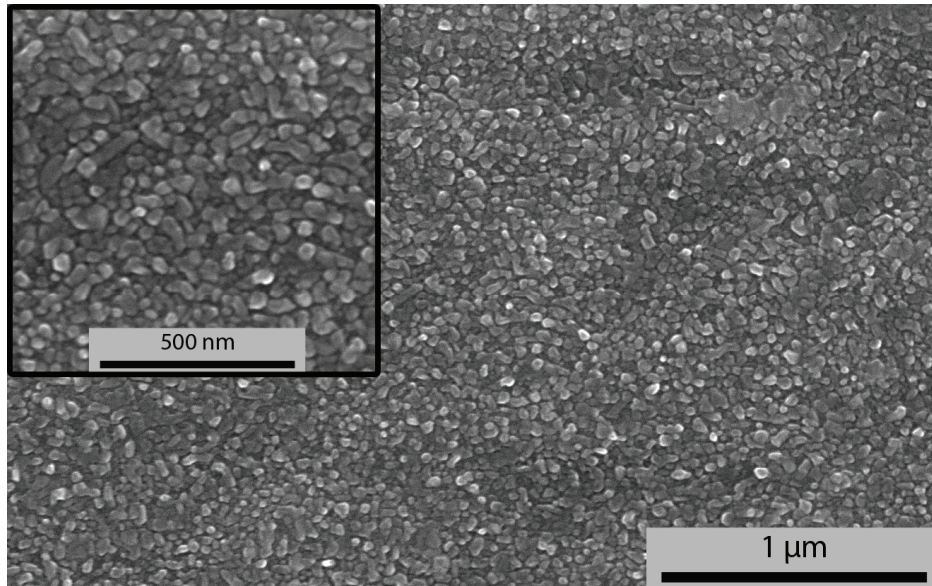
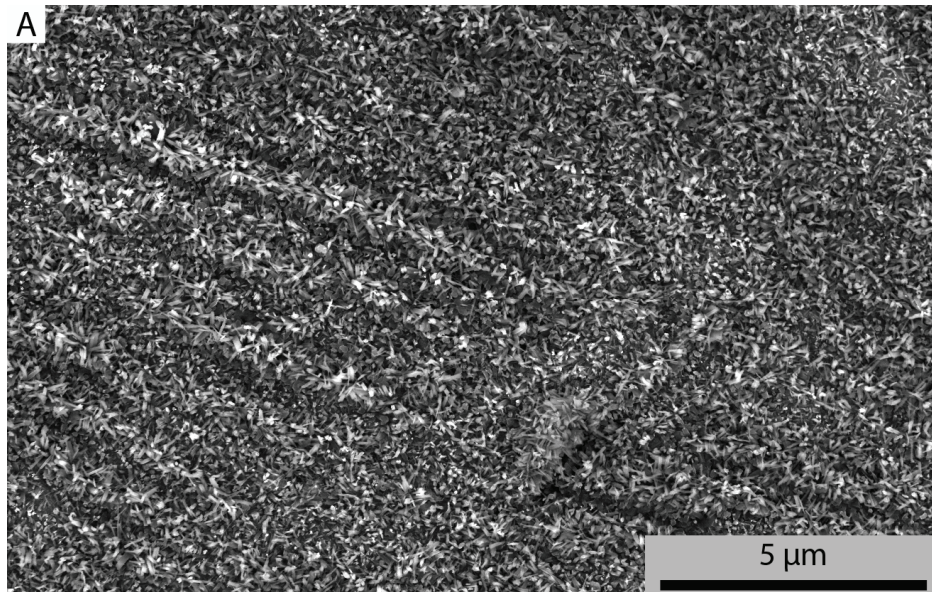


Figure 5.3: SEM micrograph showing surface morphology of a Ti64 sample oxidized at 700°C for 20 minutes in 17 ppm of oxygen.



continued

Figure 5.4: SEM micrographs of the surface of Ti64 oxidized for 45 minutes at 700°C in 17 ppm of oxygen.

Figure 5.4: Continued

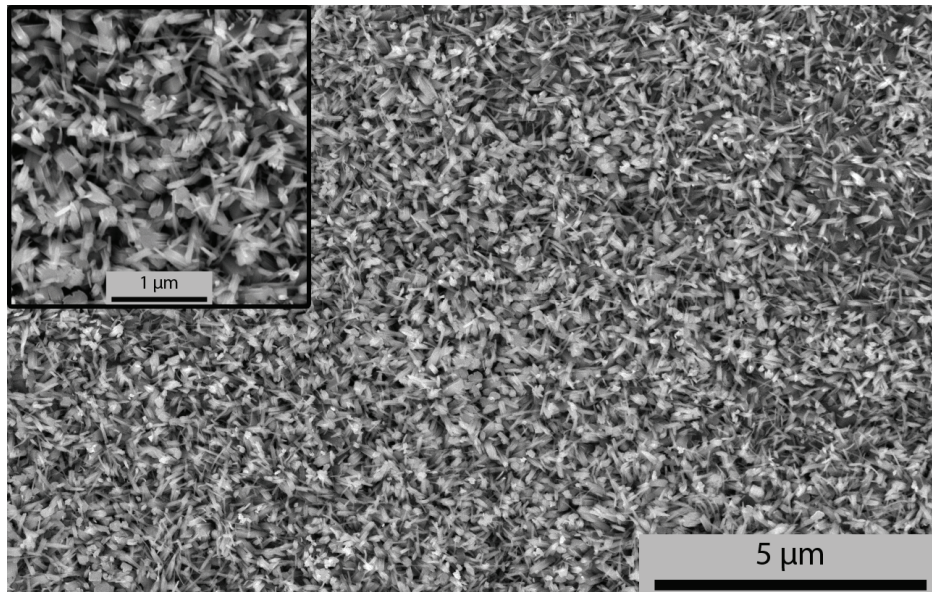
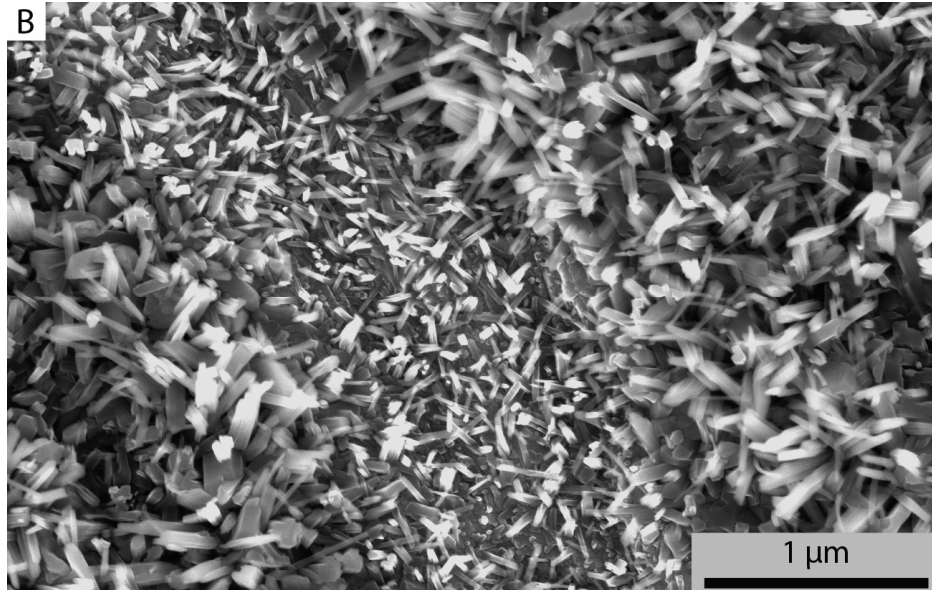


Figure 5.5: SEM micrograph of a Ti64 sample oxidized for 390 minutes at 700°C in 17 ppm of oxygen.

5.4.2.2 *Structure Determination by X-ray Diffraction*

Before proceeding with the cross-sectional analysis by TEM the samples were characterized by XRD to investigate the crystal structure of the samples at various points in the oxidation process. The results of this investigation are presented in **Figure 5.6**. The XRD pattern of the unoxidised Ti64 used in these studies is also presented in this plot for comparison. The un-oxidized sample shows the presence of both the α and β phase of titanium. The CaCO peak observed in the pattern comes from the clay used to mount the sample for XRD analysis. After 20 min of oxidation two separate oxygen containing phases are present in the sample, Ti₂O and corundum (Al₂O₃). All titanium peaks but the (101) of α phase (large peak at 40.2 2-theta) have decreased significantly. A defined shoulder has also developed on the (101) peak of α Ti due to the formation of Ti₂O. The 20 min pattern corresponds to the nanoisland morphology observed in **Figure 5.3**. At this point, no rutile peaks have been identified. At 45 min of oxidation the first peak of rutile is present but only slightly above background levels. By this point in the oxidation process NWs were already observed on the surface of the sample (**Fig. 6.4**). By 390 min, only the largest of the α titanium peaks was still present and Ti₂O was no longer observed. However, there was a significant increase in the number of rutile peaks. A significant decrease in the peak intensity was also observed for all but the (101) α titanium peak. This was not expected based on previous results and may have been a result of poor sample preparation for the XRD analysis and as such should be characterized again. Unfortunately, the XRD data was not reviewed until after the sample was coated with Au for cross-sectional sample preparation and was not suitable to be rescanned.

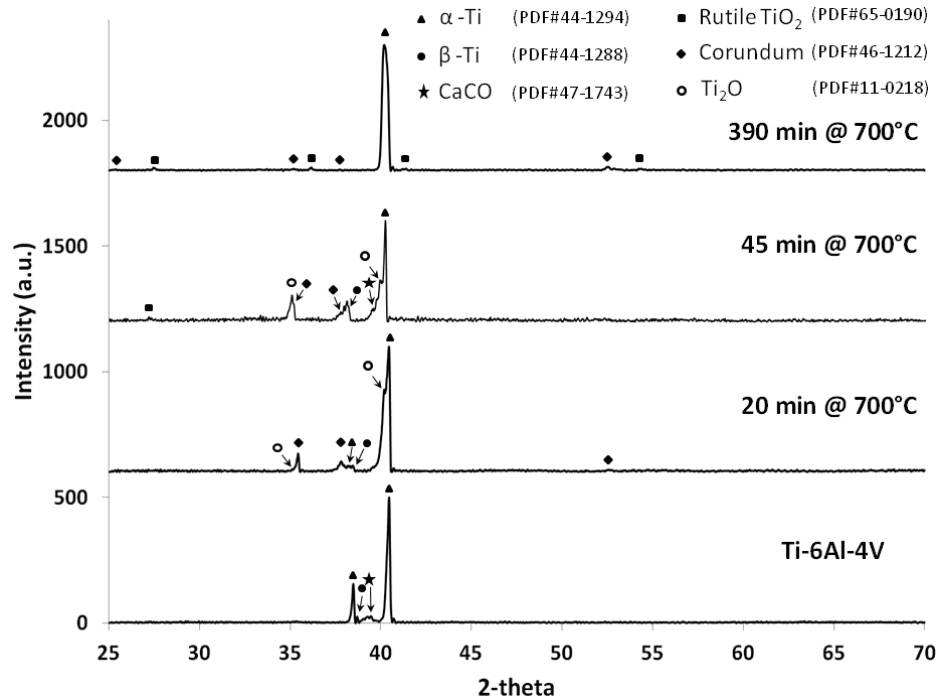
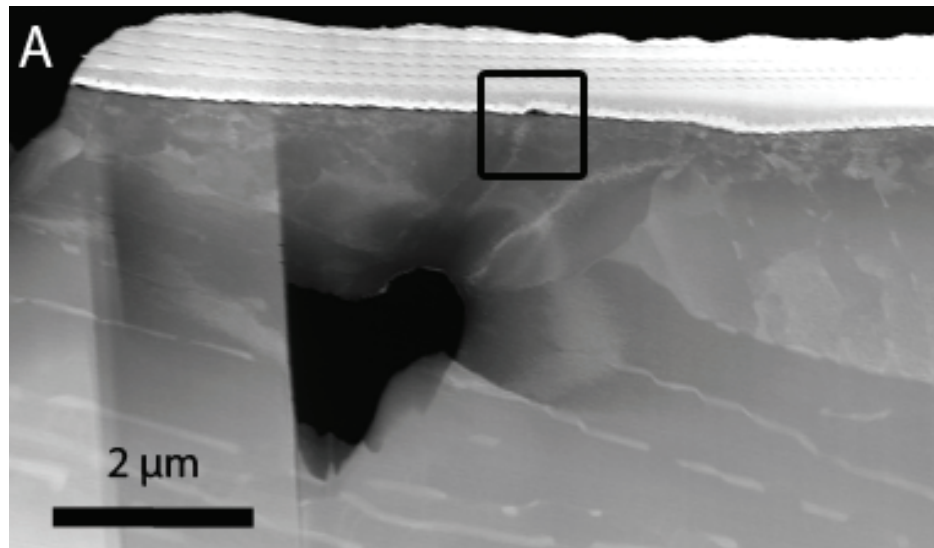


Figure 5.6: XRD analysis of Ti64 oxidized for various durations at 700°C in 17 ppm of oxygen.

5.4.2.3 *Cross-Sectional Characterization by TEM and EDS*

Cross-sectional foils were prepared by focused ion beam (FIB) milling for each of the quenched samples. Compositional profiles of the oxygen layer of the surface of the samples were obtained by EDS analysis in a TEM operating in the scanning mode. For each of the oxidation durations explored the concentration of four elements were tracked with increasing depth from the surface of the sample: titanium, aluminum, oxygen, and vanadium. **Figure 5.7** through **Figure 5.9** show TEM images of the cross-sectional foils as well as the concentration profile of these four elements as a function of sample depth as obtained by EDS.

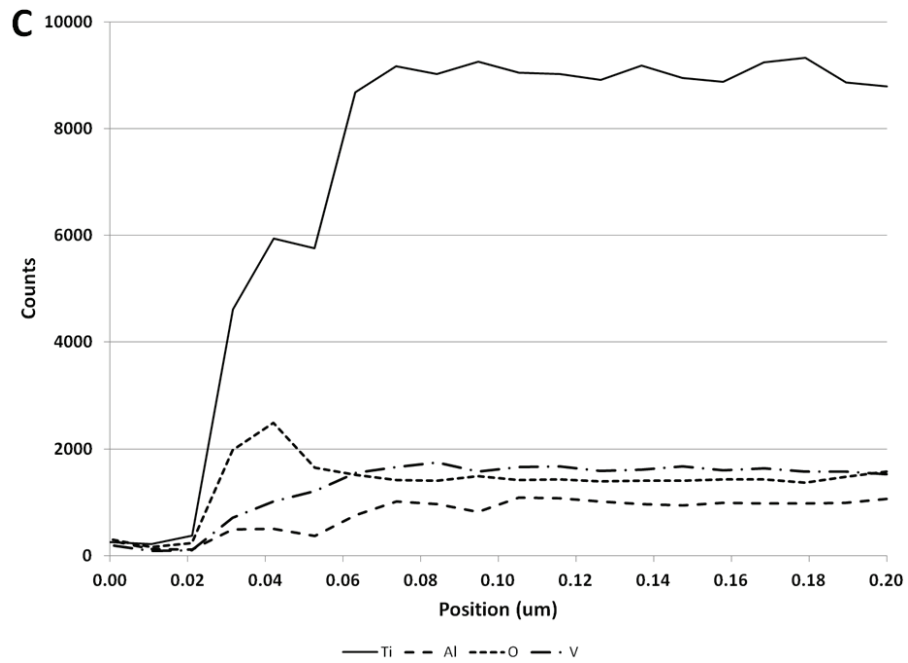
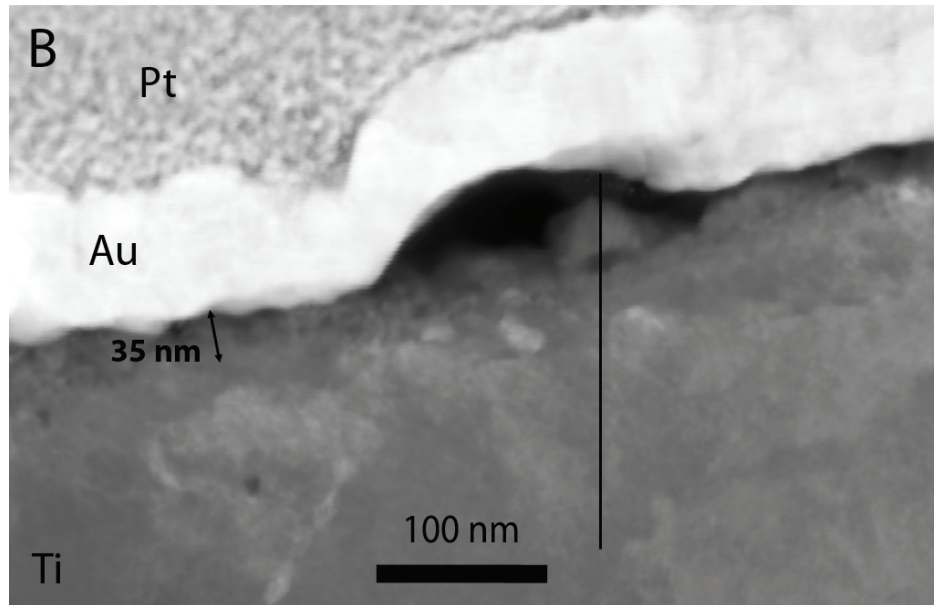
The oxide formed on the surface of the sample oxidized for 20 minutes at 700°C had an average thickness of less than 50 nm as observed in **Figure 5.7 B**. **Figure 5.7 C** shows the concentration profile for the four main elements of interest. Note that the scan started above the oxygen layer hence the negligible number of counts for all four elements until 20 nm into the sample. A significant increase in the oxygen concentration is observed in the first 30 – 40 nm of the sample indicating this is the oxidation layer. The most abundant element in the oxide layer is titanium however both aluminum and vanadium are increasing with scan depth. Titanium, oxygen, and vanadium all appear to reach a steady concentration after approximately 45 nm but aluminum does not reach a steady concentration until a depth of more than 80 nm.



continued

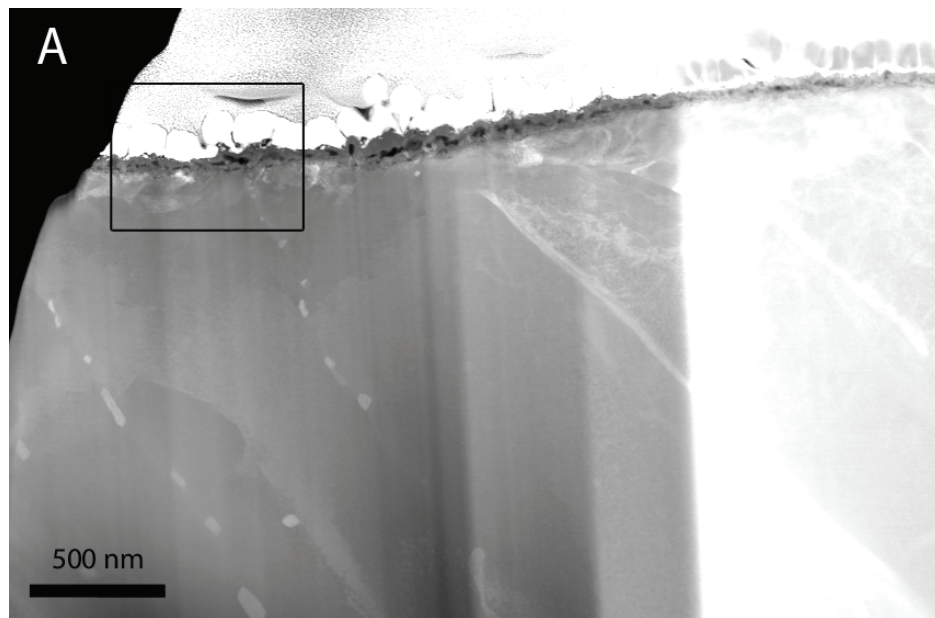
Figure 5.7: A & B) HAADF TEM images of cross-sectional sample oxidized at 700°C for 20 min in 17 ppm of oxygen. C) Concentration profiles of Ti, Al, O, and V obtained by the EDS line scan shown in B.

Figure 5.7: Continued



A cross-section view of the sample oxidized for 45 min is shown in **Figure 5.8**. After 45 minutes the oxide layer thickness increased to more than 100 nm (**Fig. 5.8 B**). The

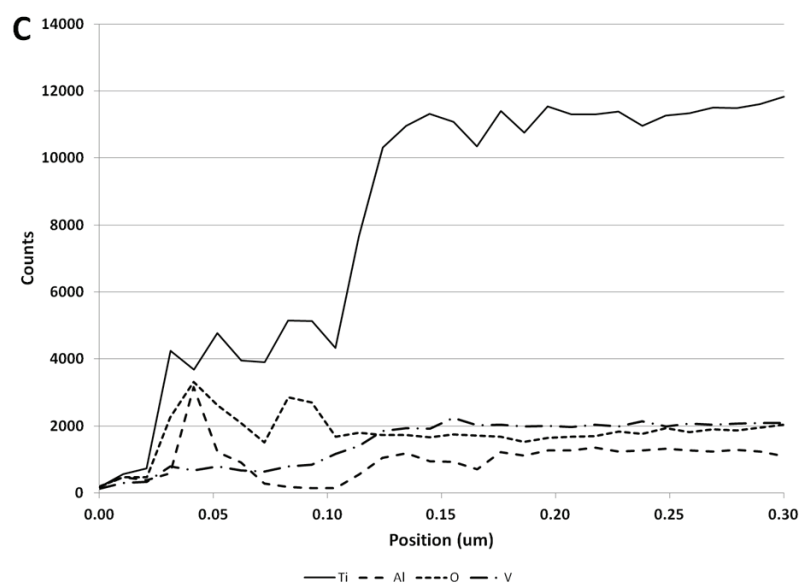
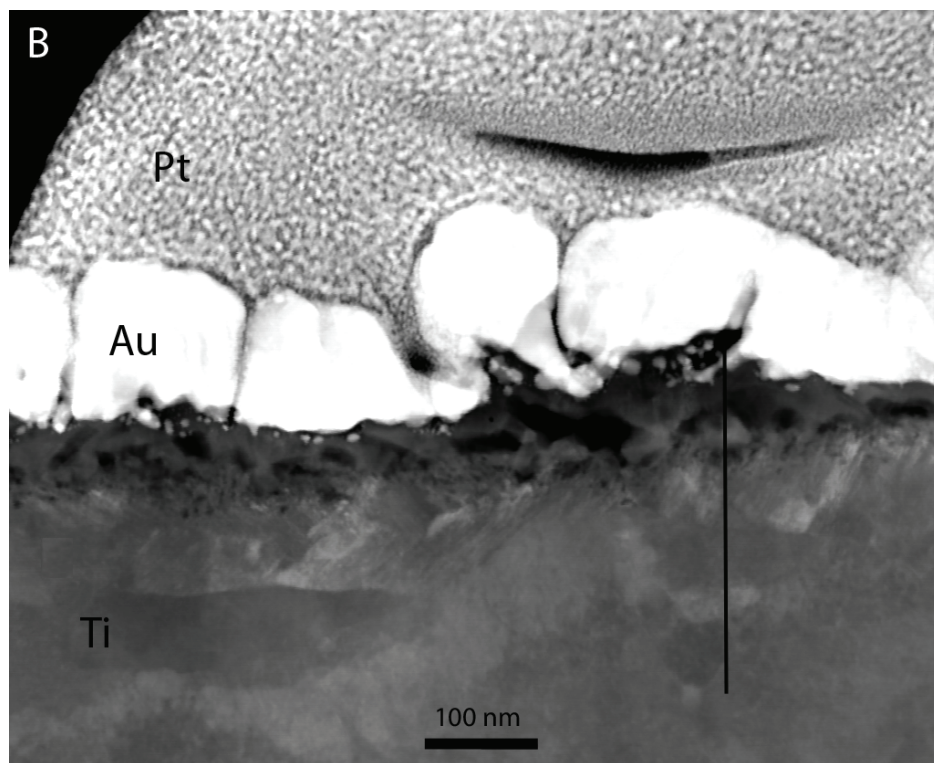
concentrations of the majority elements did not reach relatively constant values until almost 120 nm into the sample (**Fig. 5.8 C**). Similar to the 20 min oxidation sample, aluminum did not reach a steady concentration until deeper into the sample. A striking difference between the concentration profiles for this sample versus the shorter time sample is the concentration of aluminum at shallow depths. Here, immediate spikes in both the aluminum and oxygen concentrations were observed. The 20 min oxidation sample showed almost no increase in the aluminum concentration at shallow sample depths though both oxygen and titanium concentrations were relatively high.



continued

Figure 5.8: A & B) HAADF TEM images of cross-sectional sample oxidized at 700°C for 45 min in 17 ppm of oxygen. C) Concentration profiles of Ti, Al, O, and V obtained by the EDS line scan shown in B.

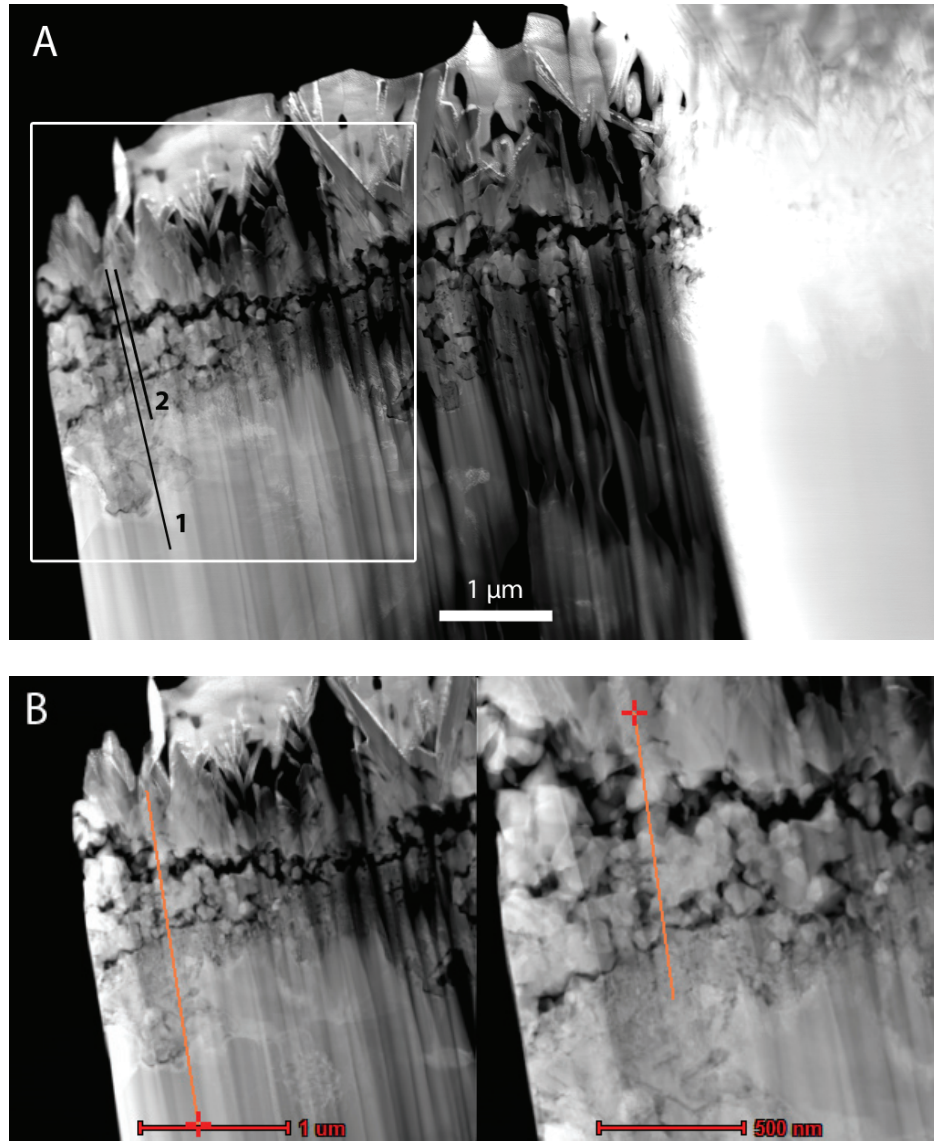
Figure 5.8: Continued



The final sample cross-sectioned for analysis by STEM and EDS was oxidized for 390 min at 700°C in 17 ppm of oxygen. The HAADF TEM images and EDS concentration profile are shown in **Figure 5.9**. This sample was oxidized for a substantially longer duration than the previous two cross-sectioned samples. As a result, the oxide layer was significantly thicker measuring more than 2 μm thick in places. Though, it should be noted that significant NW growth occurred on the surface of the sample making the starting point for the oxide thickness measurement difficult. If the tops of the NWs were selected, the oxide thickness would measure more than 3.5 μm thick. The EDS line scans on this sample were significantly longer than those in the first two samples leading to a larger distance between data points. This results in a loss of resolution for the elemental analysis. **Figure 5.9 C** shows the concentration profile collected for the line scan marked 1 in **Figure 5.9 A** and **B**. This scan started in a NW and continued 2.3 μm into the sample at a rate of 115 nm per data point to what appeared to be the metal. Due to the starting point for the scan the concentrations do not start off near zero. The concentrations of both titanium and vanadium stay rather constant throughout the scan though a slight increase in titanium is observed after the first couple of data points. At a distance of approximately 1.8 μm into the scan all concentrations appear to level off. This indicates the scan may have entered the bulk metal. The two most notable concentration profiles in this scan are the aluminum and the oxygen. The oxygen concentration starts off relatively high and decrease rather sharply after about 1.25 μm . This would indicate the oxide layer thickness in this region to be approximately 1.25 microns. The aluminum concentration is initially high but drops off to almost nothing after only 250 nm. It increases sharply at a scan

depth of approximately 1.4 μm after which it tapers off to what appears to be the aluminum concentration in the metal.

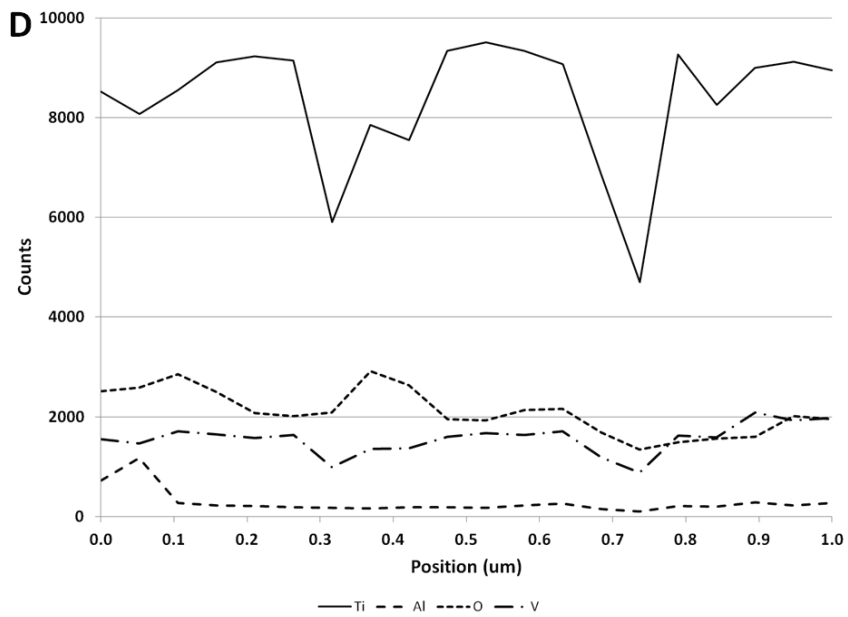
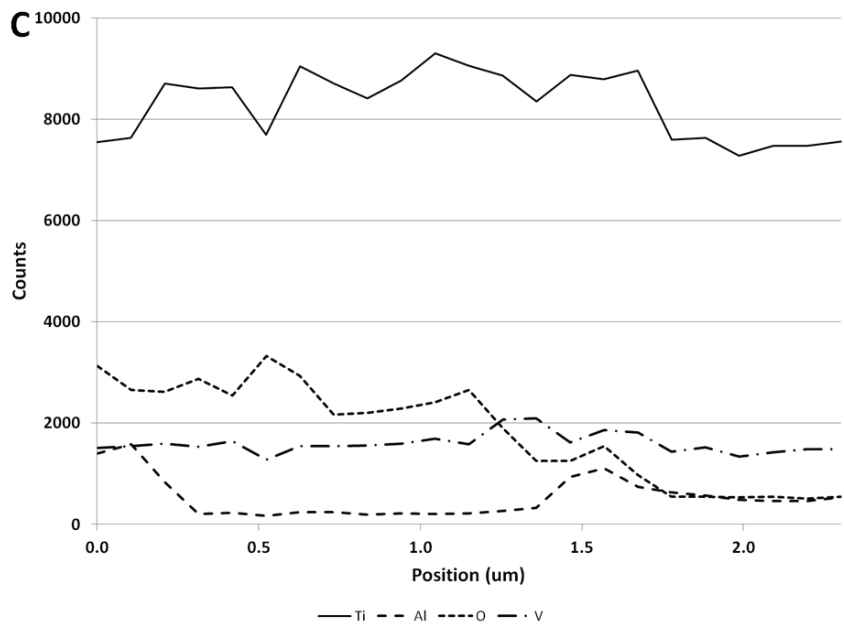
To increase the scan resolution of this region a smaller line scan was conducted. This scan is indicated by the number 2 in **Figure 5.9 A** and **B** and the compositional profile in **Figure 5.9 C**. The initially high aluminum concentration can again be observed to drop off to almost nothing after only 100 nm. The scan was not deep enough to capture the return of aluminum in the concentration profile. The titanium profile is of particular interest in this plot. Two sharp drops in the titanium concentration are observed at 300 nm and 750 nm into the scan, respectively. These correspond to the cracks visible in **Figure 5.9 B**. A depression in the vanadium concentration is also observed at these points in the concentration profile.



continued

Figure 5.9: A & B) HAADF TEM images of cross-sectional sample oxidized at 700°C for 390 min in 17 ppm of oxygen. C and D) Concentration profiles of Ti, Al, O, and V obtained by the EDS line scans, 1 and 2 respectively, shown in A and B.

Figure 5.9: Continued



5.5 Discussion of Results

All three oxidation times showed drastic differences in oxide thickness, concentration profile for various elements, oxidation by-products, and surface morphology. By comparing the results from each of the previously discussed analysis techniques a better understanding of the oxide formation and the transition from a planar oxide to 1-D growth can be developed. The remainder of this chapter is focused on this analysis and the development of a mechanism theory to describe the growth of NWs on titanium alloys by oxidation in an oxygen deficient environment.

5.5.1 Oxide Growth

Oxidation occurred very rapidly in the Ti64 samples oxidized for this investigation. This is evident in both the oxygen profile shown in **Figure 5.2** and in the progressive thickening of the oxide layer on the samples' surfaces as observed in the cross-sectional samples. There are reports in the literature that TiO₂ forms first in the oxidation of Ti64 followed by aluminum diffusion to the surface of the sample where it forms Al₂O₃.^[171] However, this is not the behavior observed for the oxidation of Ti64 in an oxygen deficient environment. Alumina and Ti₂O were the first phases to form according to the XRD analysis shown in **Figure 5.6**. Rutile was not observed in the XRD data until the 45 min oxidation sample. Based on the relative intensities of the Ti₂O and alumina peaks combined with the concentration profiles in **Figure 5.7 C** it is suggested that Ti₂O and Al₂O₃ form together with the dominant structure being Ti₂O. However at some point between 20 min and 45 min of oxidation, alumina becomes dominate oxide on the surface of the sample. This is based on the increase in the alumina peaks and a reduction

in the Ti_2O peaks as seen in **Figure 5.6** and the concentration profile in **Figure 5.7 C** where a drop in the titanium concentration is observed with a corresponding increase in aluminum concentration. Additionally, during the oxidation period between 20 min and 45 min NW growth is initiated as observed by comparing **Figure 5.3** and **Figure 5.4**. By 390 min, Ti_2O is no longer observed in the XRD analysis and only rutile and alumina remain.

5.6 Developing a Mechanistic Theory

To develop a mechanism to describe the improved growth of NWs on titanium alloys by oxidation in a low oxygen environment it is important to look at the components of the process that appear to be unique to the growth on alloys. This most notably includes the preferred growth on the β phase of titanium, improved NW yield on alloys containing aluminum, the core-shell structure of the wires, and the presence of corundum in the electron diffraction analysis of the wires. Additionally, the NW growth on alloys in the low oxygen environment is substantially improved compared to the NW on CPTi in the same environment. Thus, it is prudent to have a discussion about what impact the low oxygen concentration could have on the oxidation of a metal. The following discussion focuses on these topics culminating in a mechanism which draws upon information from experimental evidence and information from the literature. We will begin our discussion with the impact of a deficient oxygen environment on oxidation of titanium alloys.

5.6.1 Impact of Temperature and Oxygen Concentration

The growth process used to produce titania based NWs on titanium alloys by oxidation has been discussed in detail. Temperature and oxygen concentration were found to have

the greatest impact on the resulting NW morphology. Too low a temperature (below 600°C) or high an oxygen concentration (more than 250 ppm) resulted in only an oxide scale on the surface of the alloy substrates. Likewise, an extremely low oxygen concentration (below 10 ppm) or an excessively high an oxidation temperature (greater than 800°C) failed to produce NWs. Both the oxygen concentration and the oxidation temperature are known to affect the oxidation rate of titanium. Thus it can be concluded that the chemical interaction between oxygen and titanium have the greatest impact on the resulting oxide morphology. There appears to be a window or sweet spot between the oxygen concentration and temperature that can produce NWs on titanium alloys containing Al and the β phase of titanium. This window is also dependant on the surface area of the alloy sample. A greater sample surface area requires more oxygen to produce NWs at a given temperature.

It is important to note that the full range of temperatures and oxygen concentrations which are capable of producing NWs on alloy substrates have not been completely characterized. All of the temperature investigations were conducted in laboratory grade Ar with a baseline oxygen concentration of ~10 ppm. Though, these trials were often started at ambient oxygen concentrations and decreased over the course of the experiment. Likewise, oxygen concentration experiments were conducted only at 700°C. A more thorough investigation of the relationship between oxygen concentration, temperature, and NW production is warranted. However, some general conclusions can be made.

At 700°C, NWs were formed over the oxygen range of 20 - 150 ppm. However, the lower the oxygen concentrations in this range the better the NW coverage and lengths. This implies that NW growth on titanium alloys requires a deficiency in oxygen for the NWs to form. Several oxidation studies have looked at the oxidation of titanium alloys in air at 700°C but none have reported the production of NWs.[166, 169, 171] The deficient oxygen environment ensures that only the most chemically active sites on the surface of the metal oxidize. In situations where an abundance of oxygen is present, all sites for oxidation are active as there is no competition for the oxygen atoms. However, when there is a lack of oxygen only the strongest oxygen binding locations receive oxygen atoms. In conditions that produce NW growth such as 700°C in 17 ppm of oxygen the tips of the NWs appear to be the strongest oxidizing locations. This is evident in **Figure 4.13** where a Ti64 sample was oxidized in 5 ppm of oxygen at 700°C. Only small pockets of NW growth are seen. Something particular to the sites on which NW growth was observed made them more chemically active to the oxygen molecules in the gas than their surroundings. This could simply have been an effect of surface roughness as a higher surface would have more access to a flowing gas. It could also be due to a local increase in the concentration of one of the alloying elements. The strong oxidizing behavior of the tips of the NWs is also shown by the work of Dr. Lee where growth of the NWs was determined to be at the tips of the NWs.[175] The temperature step experiments shown in **Figure 5.1** show the tips of the NWs to be the strongest oxidizing location on the NWs as changes in temperature, which can be correlated to changes in the oxidation rate, resulted in changes in the NWs only at their tips. If other sites on the NWs had been as active to

oxygen as the tips a change in NW morphology would have been observed in additional locations.

Based on the understanding of diffusivities in the titanium system and diffusion in general, one could make the argument that increasing the oxygen concentration would result in an increase in the concentration gradient of oxygen between the substrate and its environment thus enhancing the driving force for oxidation. By increasing the oxygen concentration, all other factors held constant, one would increase the oxidation rate of titanium. Similarly, an increase in the oxidation temperature would increase the oxidation rate for the titanium alloy due to the increase in diffusion rates and a lowering of the activation energy required for a chemical reaction to proceed. This behavior has been observed by numerous researchers as presented in Chapter 2, Section 2.5.3.

The role of the oxygen deficient environment on the formation of NWs is to ensure only the most active oxidation sites are evolved in the oxidation process. What causes specific sites to be more active than others cannot be explained by the oxygen deficient environment as it is a product of the alloy being oxidized.

5.6.2 Impact of Aluminum

The oxygen deficient growth process works on commercially pure titanium though the NW yield is quite low compared to the alloys containing aluminum. This indicates that aluminum is not absolutely required for NW growth but when present, plays a significant role in NW formation. Aluminum, in the form of corundum (Al_2O_3), has been observed both on the surface of the alloy samples after oxidation by XRD analysis (**Fig. 5.6**) and in the structure of the wires themselves as a clad layer both by electron diffraction and EDS

analysis (**Fig. 4.6**). Although the exact role aluminum plays is not fully understood, some hypotheses can be made as to why it promotes NW growth.

It is possible that aluminum forms a surface layer of alumina (Al_2O_3) very early in the oxidation process. Alumina has been observed by XRD analysis after only 20 min of oxidation (**Fig. 5.6**), prior even to the formation of rutile TiO_2 . The working theory is that a mostly continuous layer of alumina forms inhibiting titanium access to the surface. This would limit titanium ion diffusion to grain boundaries or other defects in the alumina layer. However, once titanium ions reach the surface they would have a higher activity than the alumina layer and thus would be extremely likely to combine with the gaseous oxygen forming titanium oxide nuclei. Since titanium diffusion would be expedited in a titanium oxide compared to alumina these nuclei would act as constant sources of titanium to react with the gas. However, this would not limit the lateral growth of the titanium oxide layer. The confinement to growth in only 1-D appears to be due to an alumina layer forming on the sides of the NW. This could occur by surface diffusion of aluminum ions from the alumina layer to the titanium oxide nuclei after which reacting with gaseous oxygen to form alumina on the sides of the wire or, it could be aluminum diffusing outward from the bulk metal along the interface between the base of the titanium oxide nuclei and the alumina surface layer. In either scenario, aluminum ions would need to diffuse to the surface of the growing titanium oxide structure forming alumina and restricting the lateral growth of the titanium oxide. This is shown schematically in **Figure 5.10**.

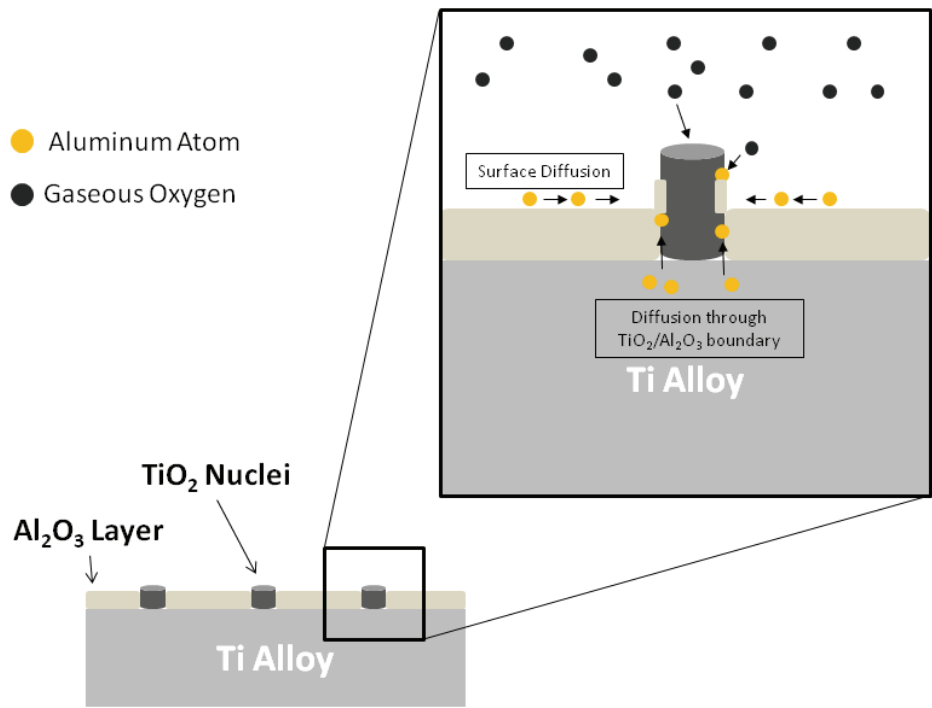


Figure 5.10: Schematic diagram showing two scenarios for aluminum diffusion to the sides of a NW to react with gaseous oxygen to form an Al₂O₃ shell layer around the TiO₂ core.

An observation from the experimental work involving the growth of NWs on titanium alloy substrates is that the initial oxygen concentration in the reaction chamber during oxidation is of critical importance and may be related to the forming of the initial Al₂O₃ surface layer. A significant drop in the oxygen concentration has been observed during early oxidation times (**Fig. 5.2**). This reduction in concentration has been attributed to fast initial oxidation of the alloy samples. If the initial concentration of oxygen in the chamber is too low, this early oxidation process which forms the alumina layer does not fully complete and NW growth is negatively affected. This was observed in the oxidation of large Ti64 foils for use in x-ray emission studies to be discussed in Chapter 6. This

negative impact of too low an oxygen concentration could be caused by insufficient formation of the alumina surface layer. If the layer is not fully formed the limiting of titanium oxidation to specific sites would not occur resulting in a reduction in the number of titanium oxide nuclei on the surface of the alloy. This would lead to a lower density of NWs as growth proceeds. Additionally, a non-continuous surface layer of alumina would not provide the constraint to small lateral dimensions of the nuclei and therefore would not promote the anisotropic growth of 1-D structures.

Thus the role of aluminum is to inhibit the formation of titanium oxide to few locations to form titanium oxide nuclei. Once the nuclei have formed, aluminum restricts the lateral growth of the nuclei by forming alumina on its sides thus limiting further growth in those directions. It is not clear why the alumina clad layer does not over take the nuclei or NW and encapsulate it in an alumina coating. Further studies are required to investigate this.

5.6.3 Impact of the β Phase of Titanium

One additional anomaly in the growth of NWs on alloy substrates versus the pure titanium substrates is the observed preference for growth on the β phase of titanium (**Fig. 4.4** and **Fig. 4.5**). This, like the impact of aluminum, has not been fully explained though some discussion and hypothetical conclusions can be made. First, it is important to realize that multiple elements of the oxidation process both on α and β titanium could be impacting the preferential growth on the β phase. For example, it has been shown that the existence of aluminum in the alloy increases the length and density of NWs but, aluminum is an α stabilizing element. Therefore, there should be significantly less aluminum in the β phase of titanium compared to α . However, some solubility of

aluminum in the β phase of titanium does exist especially if the alloy is heat treated in such a way that aluminum is trapped in the β phase upon cooling. Upon heating during the oxidation process there would be a driving force for the aluminum to leave the β phase. This could result in early formation of the alumina surface layer on the β phase compared to the α . In this way titanium oxide nuclei could form first on the β phase of titanium and thus have earlier access to the gaseous oxygen and grow for a longer time than the wires formed on the α phase. This would result in an increase in the NW length when observed after the oxidation process is stopped.

This is not the only possibility for why NW growth is more abundant on the β phase of titanium. The oxygen solubility in β titanium is significantly less than in α titanium. The decreased solubility could lead to earlier oxide formation on the β phase. The early forming oxide would have longer access to the gaseous oxygen and longer growth time compared to NWs formed on α titanium. Additionally, almost all elements involved in the oxidation process including Ti, O, and Al have been reported to have increased diffusivities in the β phase of titanium compared to the α phase.[127, 131, 181, 182] The increase in diffusivities would result in faster transport of the oxidizing species to the surface of the β phase increasing the likelihood that oxidation would occur first on β . However, there have been reports in the literature that an α layer forms first on the β grains of titanium prior to any oxide when the sample is heated in air.[154, 160, 183] These reports complicate the interpretation of the preference for NW growth on the β phase and cannot be easily dismissed. Thus, further investigation is required to fully explain the preference for NW formation on the β phase of titanium.

5.6.4 Transition from Planar Oxide to Nanoislands

The transition from planar growth to nanoisland formation is an important component to understanding of the mechanism responsible for NW production on titanium alloys containing aluminum. It is important to note that the cracked oxide layer Dr. Lee observed and labeled “stage 1” in his proposed growth mechanism was not observed in the more recent findings reported in this document. This is not to say Dr. Lee’s findings are incorrect. Rather it is more likely that the short time oxidation trials conducted for cross sectional analysis were too long of oxidation durations to capture this phenomena. That is, the cracked layer had already converted to nanoislands in the shortest time interval investigated. Additionally, Dr. Lee did not observe nanoisland formation until after 1 hour of oxidation while they were observed after only 20 min in the present study and by 45 min, NW growth was observed. The main difference in the experimental work between the current study and Dr. Lee’s was the alloy composition. Dr. Lee used the metastable β phase alloy Ti 5%Al-5%V-5%Mo-3.5%Cr-0.5 %Fe while the current study focused mainly on the $\alpha + \beta$ alloy Ti 6%Al-4%V. The difference in the oxidation duration required to produce nanoislands may be attributed to the effect of the additional alloying elements in the Ti5-5-5 alloy have on oxide formation. Molybdenum and chromium are often added to titanium alloys with the intention of suppressing oxide formation at high temperature.[97] Iron has also been reported to decrease the diffusion of many substitution elements in titanium including aluminum.[123] The reduction of both the oxide formation and the diffusion of aluminum to the surface of the sample could be impacting the oxidation duration required to transition from the cracked oxide layer to nanoislands. Since Ti64 does not contain Mo, Cr, or Fe in significant

concentrations the oxide layer formation may be considerably faster. Additionally, since the diffusion of Al would not be slowed by Fe an alumina surface layer may form faster on Ti64 leading to earlier nanoisland formation. The rationale for this argument is presented in the following paragraph.

To begin, aluminum has an extremely high affinity for oxygen much like titanium. Therefore, it will react with oxygen to form an oxide whenever possible.[171] This is especially true for oxidation at high temperature. The fact that aluminum is only present at an average level of 6 at. % in the alloys tested and yet an Al_2O_3 layer was detected by XRD analysis after only 20 min of oxidation at 700°C is evidence of its propensity to form. Additionally, Al_2O_3 was observed on the oxidized samples prior to rutile TiO_2 . If a corundum layer forms on the surface of the alloy very quickly in the oxidation process it could limit the oxygen available to react with titanium. Although the solubility of titanium in alumina is extremely low, titanium ions would still be able to diffuse outward from the bulk to the surface through grain boundaries or other defects in the Al_2O_3 surface layer. When they reach the surface, the Ti ions would have a higher chemical activity than the surrounding alumina and could react with gaseous oxygen forming titanium oxide. In this way, small sprouts or islands of titanium oxide could form on the alumina surface layer. This explanation would suggest that aluminum aids in NW formation by providing a physical barrier to planar titanium oxide growth at least in the early stages.

5.7 Mechanism

By combining the concepts discussed in the preceding sections a more formal growth mechanism can be presented to explain the formation of NWs on titanium alloy samples containing aluminum when oxidized in an oxygen deficient environment. Though no direct experimental evidence showed the formation of the cracked oxide layer described by Dr. Lee it is assumed to still be present as the initial stage of oxide formation and as such will be presented as part of the proposed growth mechanism.

The formation of NWs on titanium alloy substrates begins with the initiation of a cracked oxide layer (**Stage I**). The exact composition of this layer is not yet known but is most likely a combination of Ti_2O and Al_2O_3 based on the XRD results for short time oxidation samples. This is followed by the formation of a continuous surface layer of alumina by outward diffusion of aluminum from the bulk to the surface where it reacts with gaseous oxygen to form Al_2O_3 (**Stage II**). The continuous alumina layer slows the oxidation of the bulk titanium by limiting oxygen transport to the base metal. Titanium atoms will diffuse to the surface of the alumina layer through grain boundaries and other defects in the alumina layer. The titanium atoms which reach the oxide surface will have a much higher chemical activity than the surrounding alumina and will react with the gaseous oxygen present in the oxidizing environment forming titanium oxide nuclei (**Stage III**). Titanium can readily diffuse through the titanium oxide and as such is constantly supplied at the growth front of the forming oxide nuclei. This process of titanium outward diffusion from the bulk to the growth front of the oxide nuclei will continue as long as the sample remains at elevated temperature. Simultaneously, aluminum atoms will also be diffusing outward from the bulk alloy. Aluminum diffusion

in Al_2O_3 has been reported to be much slower than in titanium thus the fastest diffusion path for the aluminum atoms would be the boundary between the titanium oxide nuclei and the alumina surface layer.[127, 184] This results in aluminum atoms on the sides of the growing titanium oxide nuclei. An alternate diffusion path for the aluminum atoms is by surface diffusion along the alumina surface layer to the titanium oxide nuclei. In either case, the aluminum reacts with the gaseous oxygen forming Al_2O_3 on the sides of the titanium oxide nuclei limiting further lateral growth of the nuclei (**Stage IV**). As this process continues, Ti atoms are supplied to the growth front of the titanium oxide while Al atoms are supplied to the sides of the titanium oxide. Thus, growth is inhibited on the sides of the titanium oxide but not at the tip. This results in the growth of titanium oxide in only the vertical dimension. As the oxidation time increases the titanium oxide continues to grow vertically until highly anisotropic oxide nanostructures are formed (**Stage V**).

The previously outlined mechanism involves five stages of growth shown schematically in **Figure 5.11** and summarized as follows. **Stage I**: Formation of a cracked oxide layer on the surface of the titanium alloy when exposed to an oxygen deficient environment at elevated temperatures. **Stage II**: Formation of a surface layer of Al_2O_3 which slows the oxidation of the titanium alloy. **Stage III**: Formation of titanium oxide nuclei by the diffusion of titanium to the surface through grain boundaries or other defects where it reacts with gaseous oxygen. **Stage IV**: Continued growth of the titanium oxide nuclei while simultaneously aluminum atoms diffuse to the sides of the nuclei where they react with gaseous oxygen forming Al_2O_3 and inhibiting lateral growth of the nuclei. **Stage V**:

Continued oxidation of titanium at the nuclei surface and simultaneous formation of Al_2O_3 on the sides of the titanium oxide inhibiting lateral growth and promoting the formation of highly anisotropic core-shell nanostructures.

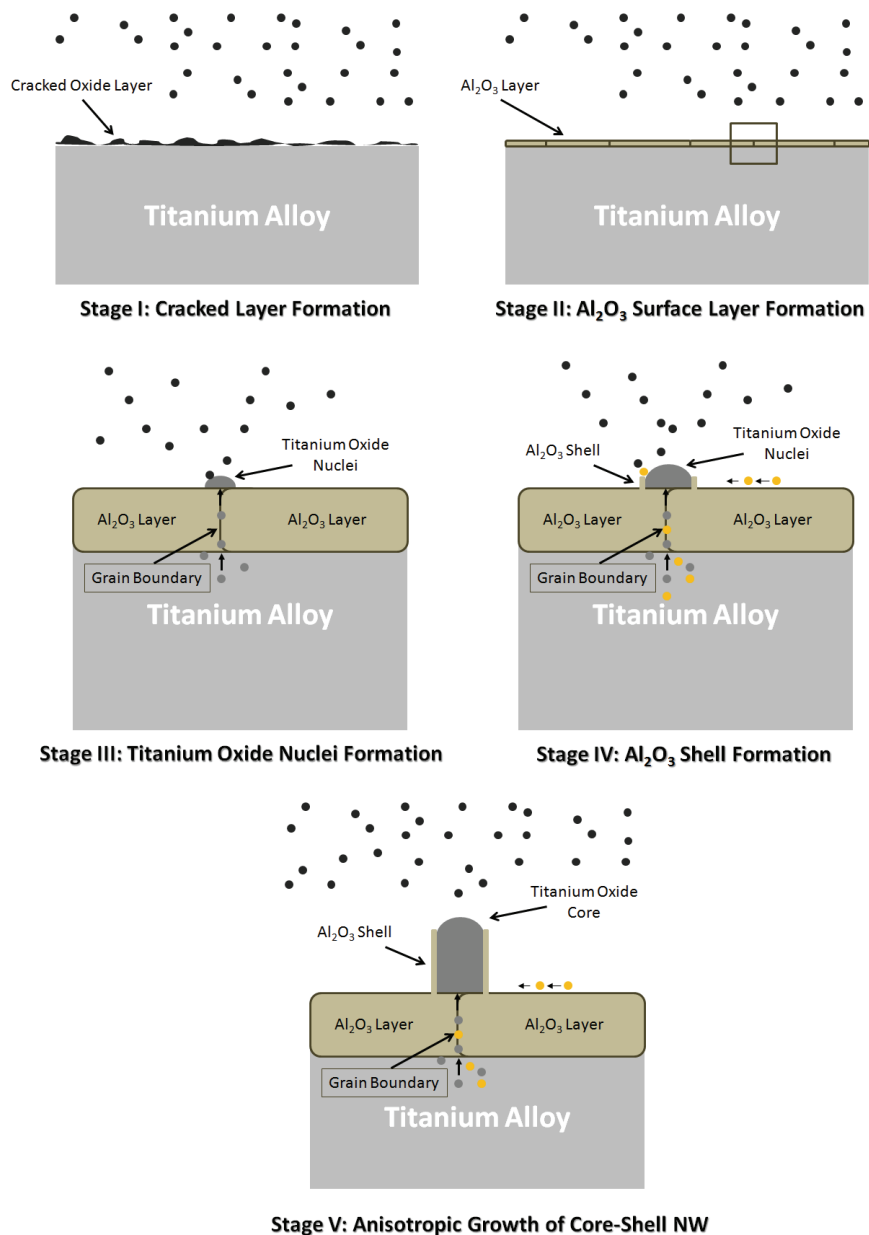


Figure 5.11: Schematic representation of the 5 stages involved in the growth of 1-D nanostructures on titanium alloys by oxidation in an oxygen deficient environment.

5.8 Conclusions

A mechanism theory to explain the formation of core-shell NWs on titanium alloys containing aluminum by oxidation in an oxygen deficient environment was presented. The theory was based heavily on experimental results as well as information reported in the literature for the diffusion and oxidation behavior of Ti64. The respective contributions of Lee and the present author are presented in **Table 5.1** for clarity. The role of aluminum in the NW formation is to inhibit lateral growth of the NWs by forming a layer of Al_2O_3 on the sides of the NW. Additionally, an alumina surface layer which forms early in the oxidation process slows the oxidation of the titanium substrate limiting the titanium oxide growth to small nuclei formed by titanium diffusion along defects in the alumina layer. Although the presence of aluminum and the β -phase of titanium have been shown to improve NW yield, neither are required to produce nanowires.

There are still gaps in the understanding of the growth process. The first stage of growth involves the formation of a cracked oxide layer however the oxide make-up of this layer is unknown. XRD analysis suggests that it may be a combination of Ti_2O and Al_2O_3 but further studies are required to confirm this.

With the successful optimization of a process to produce NWs on Ti alloy substrates the next logical step was to investigate methods for improving NW growth on CPTi substrates. This would allow for the growth of NWs on wider range of Ti materials thus increasing is potential as a useful technique for a variety of applications and industries. The following chapter focuses on the development of an adaptation to the above process that allows for large scale NW growth on CPTi.

Researcher		Mechanism Formulation			
Lee [174]	Questions Investigated	Question 1	Question 2	Question 3	Investigation Techniques
Key Findings	<ol style="list-style-type: none"> 1. Are catalyst present to promote 1-D growth? 2. Does NW growth due to bulk diffusion or vapor deposition? 3. Does Growth occur at NW tip or base? 	No catalyst elements were identified via SEM, TEM, and EDS analysis	<ul style="list-style-type: none"> • Vapor pressure of Ti and Ti oxides was too low to supply sufficient source material. • Growth occurred by bulk diffusion 	Multi temperature step oxidations showed growth to occur at NW tip	<ul style="list-style-type: none"> • Short time oxidation • SEM characterization of oxidized samples for surface morphology
Current Study	Questions Investigated	Question 1	Question 2	Question 3	Investigation Techniques
Key Findings	<ol style="list-style-type: none"> 1. What promotes transition from cracked oxide to nanoislands? 2. What promotes 1-D growth? 3. Why is lateral growth inhibited? 	<ul style="list-style-type: none"> • No cracked layer was observed. • Transition is due to oxide scale which limits oxidation to only highly active sites 	Initial growth of Al ₂ O ₃ layer limits Ti oxidation to Ti ions diffused through defects in Al ₂ O ₃ layer which form Ti-O nuclei	<ul style="list-style-type: none"> • Al ions diffuse to sides of Ti oxide nuclei and form Al₂O₃ • This passivates the sides of the Ti oxide promoting 1-D growth 	<ul style="list-style-type: none"> • Short time oxidation based on O₂ profile • SEM & XRD surface characterization • Cross-sectional characterization via TEM and EDS

Table 5.1: Contributions of respective researchers to the mechanism investigation for the growth of TiO₂ NWs by oxidation in an oxygen deficient environment.

Chapter 6: Growth of TiO₂ Nanowires on Commercially Pure Titanium (CPTi)

6.1 Introduction

Previously, a method for the growth of TiO₂ nanowires (NWs) on Ti alloy substrates was developed by Lee and discussed in the preceding chapter.[176] Lee's process was optimized to produce uniform NW coverage on a range of Ti alloy substrates and configurations. However, it was less successful at producing well defined NWs on commercially pure Ti (CPTi) samples. At the optimal growth conditions for the alloy samples, the oxidation of CPTi only produced very small (~300nm) NWs as seen in **Figure 6.1**. By consulting the relevant oxidation literature for titanium a possible improvement to the nanostructured oxidation process for CPTi was identified.

Numerous studies have investigated the oxidation behavior of titanium metal in a variety of oxygen environments. Several of these studies looked at the impact of humidity on the oxidation of CPTi. Pe' rez studied the oxidation behavior of Ti in both dry air and humid environments.[173] He reported that at temperatures between 600-650°C the Ti oxidation behavior was controlled by rutile TiO₂ growth while at higher temperatures, the oxidation rate was controlled by the dissolution of oxygen. While comparing the effects of water vapor and dry air on the oxidation rate of CPTi it was found that at temperatures near 700°C, the addition of water vapor increased the oxidation rate of Ti. However as time

increased, a multilayered oxide developed and samples oxidized in the presence of water vapor showed decreased oxidation rates at long oxidation times compared to samples oxidized in dry air. If averaged over long times, the total mass gain of pure titanium oxidized in water vapor at 700°C was nearly the same as samples oxidized in air. However, the resulting rutile layer grew as a more dense oxide scale. Motte *et. al.* also investigated the oxidation behavior of CPTi in the presence of water vapor.[185] Their results also indicated an increase in the Ti oxidation rate for relatively short times in the presence of water vapor. Furthermore, through SEM characterization of oxide scales formed in the temperature range of 650-850°C they noted the formation of whiskers. The existence of whiskers was attributed to stresses existing in the oxide scales formed in water vapor.

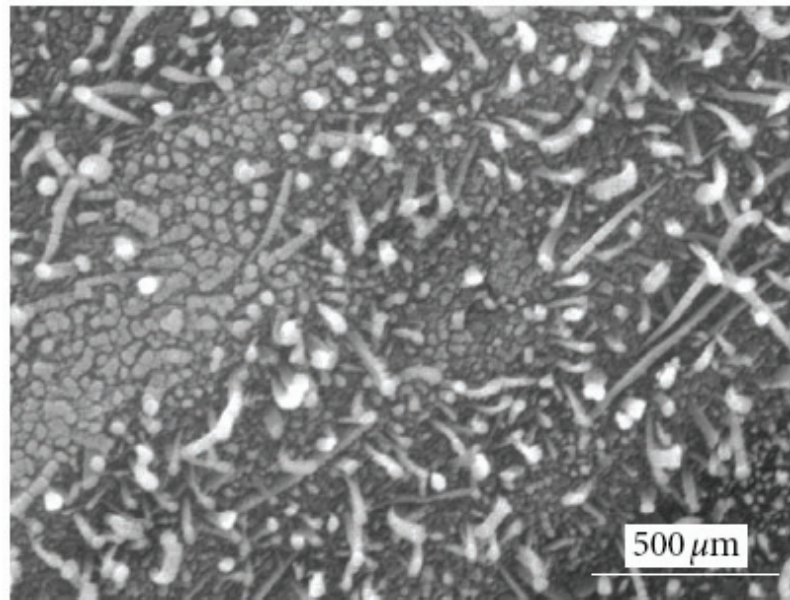


Figure 6.1: SEM micrograph of NWs grown on CPTi metal at 600°C for 8hrs in a low oxygen environment.[176]

Whiskers, also described as wires, have been reported in other oxide systems where oxidation occurred in a humid environment. Xu *et. al.* reported on the growth of CuO NWs by oxidation in a variety of oxygen environments.[78] They grew CuO NWs by oxidizing copper foils in air and oxygen environments over the temperature range of 400-500°C. It was found that the addition of water vapor during oxidation increased both the length and yield of the CuO NWs. These works prompted the investigation of the improvement of NW yield on CPTi by introducing water vapor during oxidation.

6.2 Experimental

Commercially pure Ti foil (Ti Foil 99.99%+, Alfa Aesar), Ti TEM grids (Ti 300 mesh, Ted Pella), and powder (Ti powder –325 mesh 99.98%, Sigma Aldrich) were used for the CPTi oxidation experiments. Foil samples were cut using a diamond cutter (LECO, part number 801-136) and mechanically polished using SiC sand paper (1200 grit). After polishing, all samples were cleaned by the following procedure including a rinse in deionized (DI) water between each step: 1) 5 min ultrasonication in acetone, 2) 5 min ultrasonication in methanol, and 3) 5 min ultrasonication in DI water. The samples were inserted into a quartz tube (OSU Glass Shop) which was then placed in a horizontal tube furnace (Lindberg, TF55035A) for gas heat treatments. The oxidation environment was set by flowing laboratory grade Ar (99.998%) at a target flow rate maintained by a digital gas flow meter(s) (C100L, Sierra). Humidity was introduced by passing the flowing Ar through a bubbler filled with 150 ml of deionized water (DI). This method of introducing humidity will be referred to as “wet argon” here after. **Figure 6.2** shows a schematic of the experimental setup. Ti TEM grid samples were oxidized vertically by placing them in

a 1'' x 2'' x 0.25'' piece of bulk Ti in which a slit had been cut approximately 1 mm deep using a diamond saw. Where applicable, the oxygen partial pressure in the gas was monitored by an oxygen sensor (ZRO2000, Alpha Omega Instruments). The humidity level was monitored using a dew point transmitter (EE31-PFTE, E+E Elektronik Corporation). The furnace temperature and gas flow rate were computer controlled through an instrument control and data acquisition LabView program written in-house.

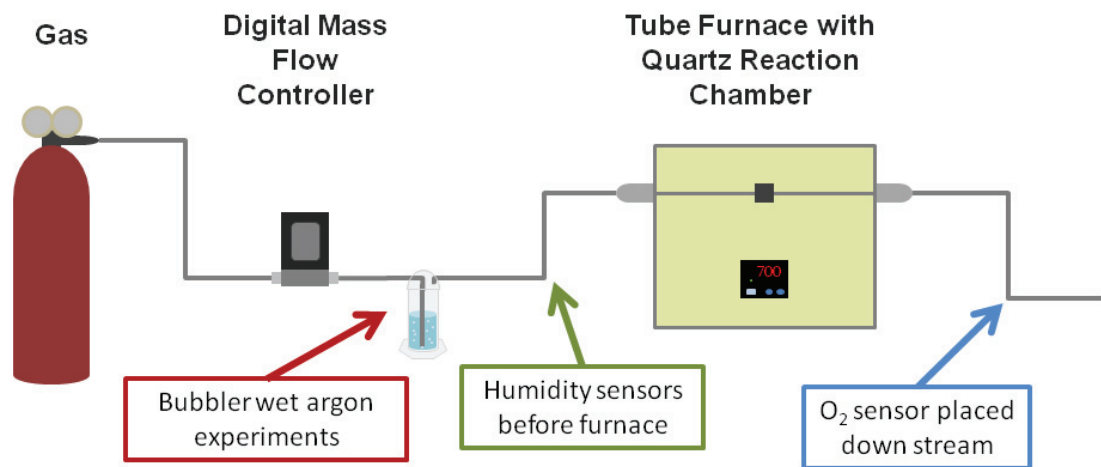


Figure 6.2: Schematic showing experimental setup used in the oxidation experiments using a humid environment.

Surface morphology was characterized in a high resolution FEG-SEM SEM (Model Sirion, FEI, Oregon). Prior to SEM characterization, most samples were coated in a thin layer of Au using a sputter coater (Model 3 Sputter Coater 91000, PELCO) at a plasma current of ~15mA for 40 seconds. Those samples not coated were placed in a clip style mount for imaging via SEM. The clip mount was used when further processing of the

sample after SEM analysis was necessary. Crystal structure verification was performed using XRD analysis (Scintag PAD-V and Bruker XD). The structure of the resulting NWs was examined with a transmission electron microscope (TEM, Model CM200, FEI). Elemental analysis of individual NWs was performed by electron dispersive spectroscopy (EDS).

6.3 Results and Discussion

6.3.1 Initial Results

As a first approach to this investigation the optimized growth parameters for the production of TiO₂ NWs on Ti alloy samples, as discussed in the conclusion of Chapter 4, were used. A CPTi foil sample was oxidized at 700°C for 8 hours under 500 sccm flowing Ar bubbled through 150 mL DI water (wet argon). **Figure 6.3** shows an SEM image of the resulting NWs. Comparing these results to those in **Figure 6.1** a drastic increase in the length of the as grown NWs can be seen for the wet argon oxidation. An in-depth investigation into the growth parameters and an exhaustive characterization of the NWs were conducted. For all oxidation experiments for CPTi conducted in wet argon, a variety of nanostructures formed including wires, ribbons, and pillars or rods. In this chapter, when referring directly to the wire-type morphology the term nanowires (NWs) will be used. When discussing or referring to all structures formed independent of shape, the term nanostructures will be used. Likewise, when referring to a specific nanostructure shape other than wires, the appropriate term will be used.

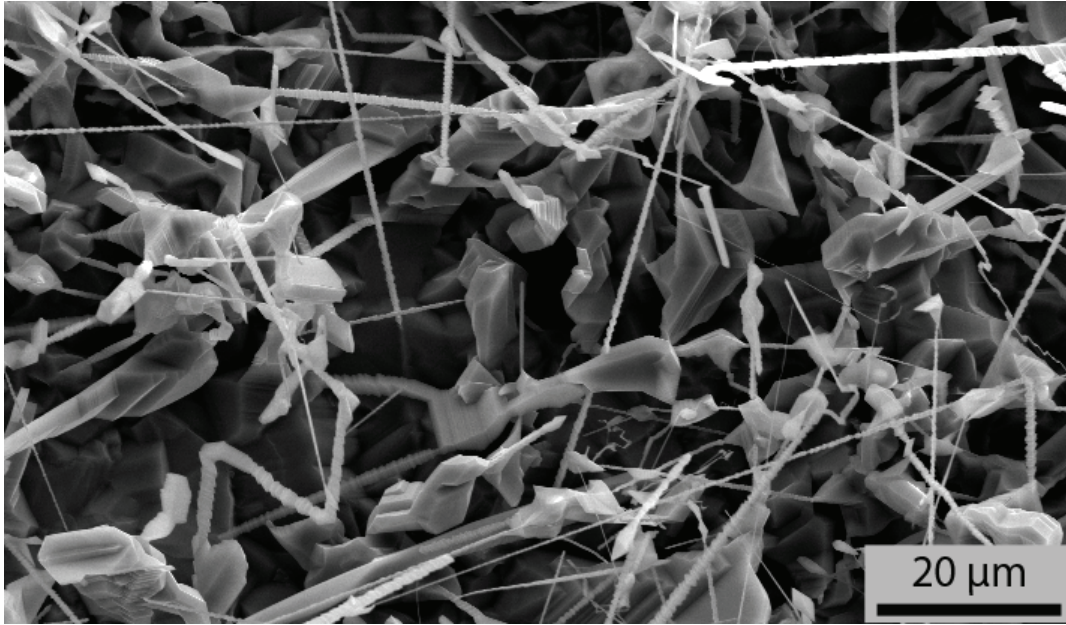


Figure 6.3: SEM image of nanostructured oxide growth resulting from the oxidation of CPTi foil in wet argon.

6.4 Growth Parameter Investigation

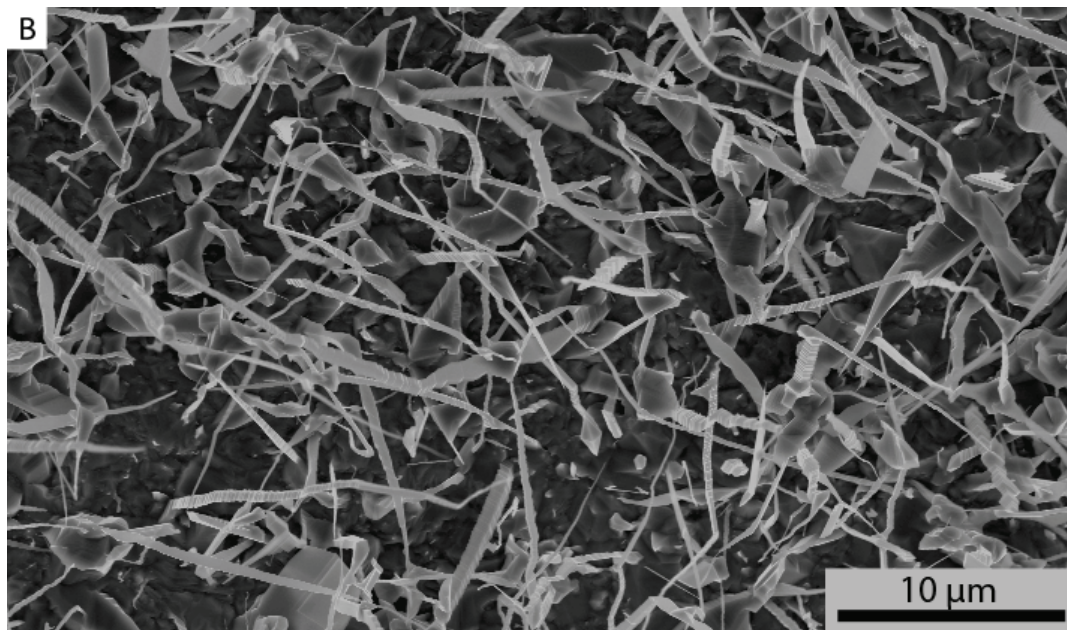
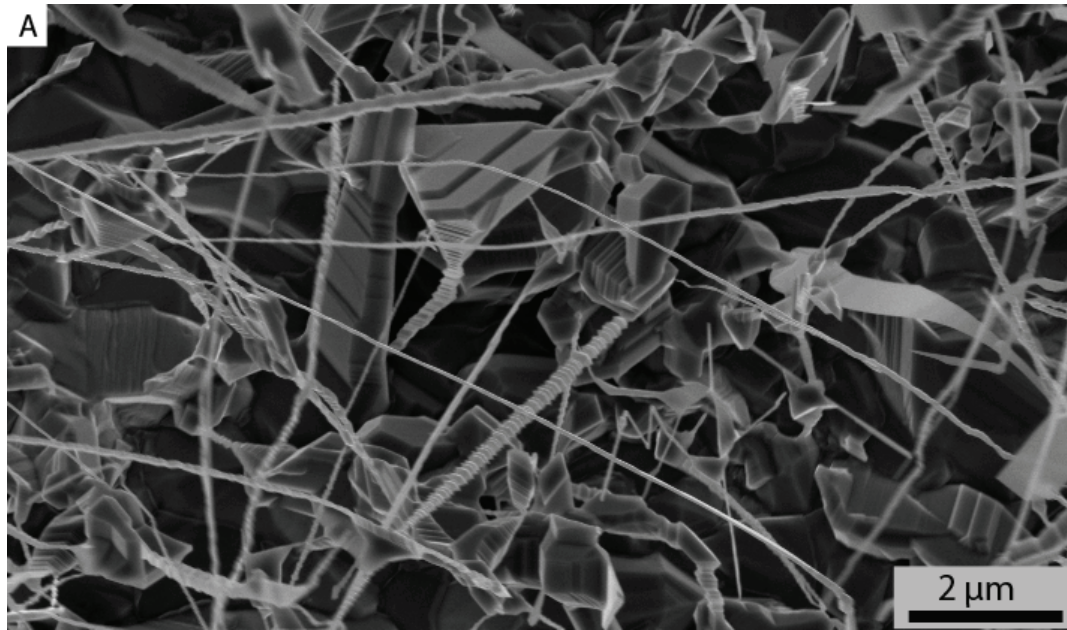
Initial results from the oxidation of CPTi foil in wet argon showed great promise as a means of improving the NW yield. The parameters used in the initial test were taken directly from the nanostructured oxidation work on the Ti alloy substrates. These parameters while optimized for the alloys may not be the optimal conditions for producing NWs on CPTi.

6.4.1 Effect of Temperature

The work of Motte *et. al.* demonstrated that whiskers of TiO_2 could be formed by oxidation in a humid environment over the temperature range of 650-850°C.[185] Based on this information and the desire to obtain the optimum growth temperature for the production of NWs on CPTi substrates, samples were annealed at temperatures between

500°C and 850°C under flowing Ar bubbled through DI water. **Figure 6.4** shows selected results from these experiments. A significant difference in NW coverage was not observed however as the temperature increased, both the length and diameter of the NWs increased. For all temperatures, a variety of nanostructures formed including wires, pillars, and ribbons. For the following diameter and length measurements only wires were measured and an average was made over a minimum of 20 wires. Samples oxidized at 600°C had an average NW diameter of 150 nm while those oxidized at 800°C had an average of more than 2 μm . For comparison, the average lengths of the NWs in the 600°C and 800°C oxidation sets were 28 μm and 39 μm , respectively. In the case of the wires grown at temperatures above 800°C a mix of nano and micron scale wires were observed.

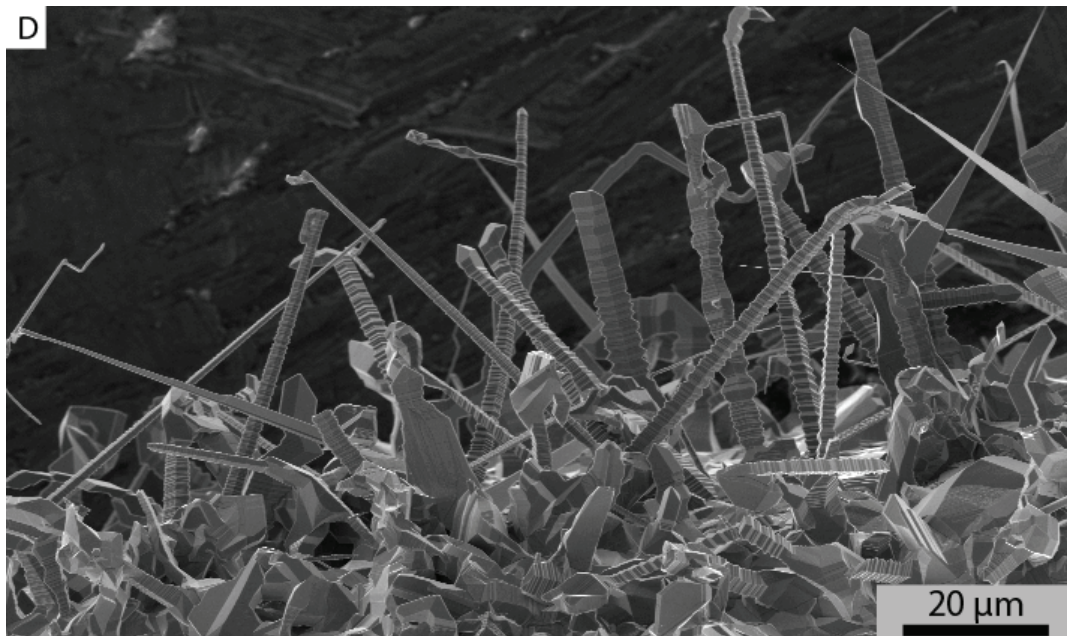
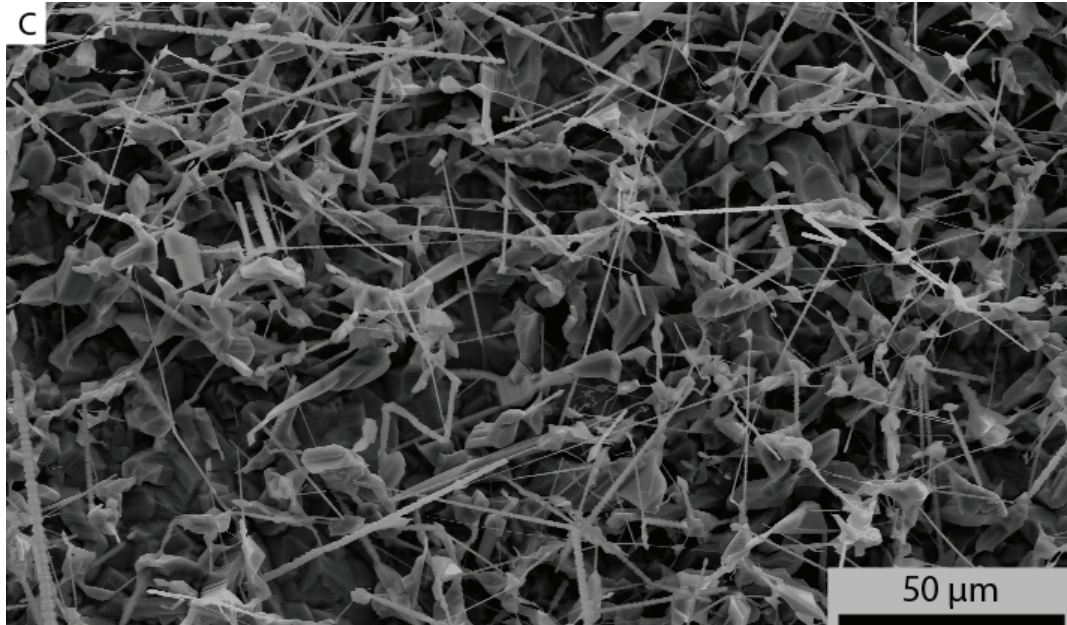
No one temperature could be identified as the optimum temperature for the production of NWs on CPTi due to the lack of direct correlation of NW coverage with oxidation temperature. It was seen that as the temperature increased, the average length and diameter of the resulting NWs increased but the overall coverage remained relatively constant. The flow rate of the wet argon was also thought to play an important role in the NW formation due to its direct relationship to the amount of water vapor introduced into the reaction chamber.



continued

Figure 6.4: SEM micrographs showing the results of wet argon oxidation experiments on CPTi foils for 4 hours at A) 600°C, B) 700°C, C) 750°C and D) 800°C.

Figure 6.4: Continued



6.4.2 Effect of Flow Rate

Due to the potential influence the flow rate could have on the humidity level in the reaction chamber, multiple flow rates were investigated for the oxidation of CPTi.

Additionally, since NWs were observed over a range of annealing temperatures each flow rate investigated was tested at multiple oxidation temperatures. **Figure 6.5** is a comprehensive representation of the nanostructures obtained at different combinations of flow rate and temperature. It should be noted that Ar flow rates of 300 sccm, 500 sccm and 750 sccm bubbled through DI water produced average relative humidities of 96%, 93%, and 82% respectively in the reaction chamber. Multiple combinations of gas flow rate and oxidation temperature were successful at producing nanostructures. For example, all flow rates tested produced NWs on the CPTi foils over the temperature range 700-750°C while at 600°C only a flow rate of 750 sccm produced NWs. Oxidation at 800°C under all flow conditions explored produced a mixture of both nanometer and micron sized structures. Through this set of experiments a trend in the impact of flow rate on the resulting oxide morphology is evident. At low flow rates (300 sccm) the oxidation process produces a relatively small coverage of nanostructures compared to higher flow rates. As the flow rate increased, a corresponding increase in the nanostructure coverage was observed. Additionally at high flow rates (750 sccm), an increase in the nanostructure's size was also observed. This increase in size was dramatically larger at higher temperatures. In the case of oxidation at 800°C under 750 sccm of flow the structures formed were not of nano-scale but rather were microns in diameter and 10s-100s of μm in length. It is important to note that while both the size and diameters of the nanostructures (specifically NWs) increased, the shape and morphology of the nanostructures appeared to remain consistent with that of the structures grown at both lower temperature and flow rate. This indicates that the mechanism(s) governing the

growth process have not changed but rather an increase in the growth kinetics has occurred.

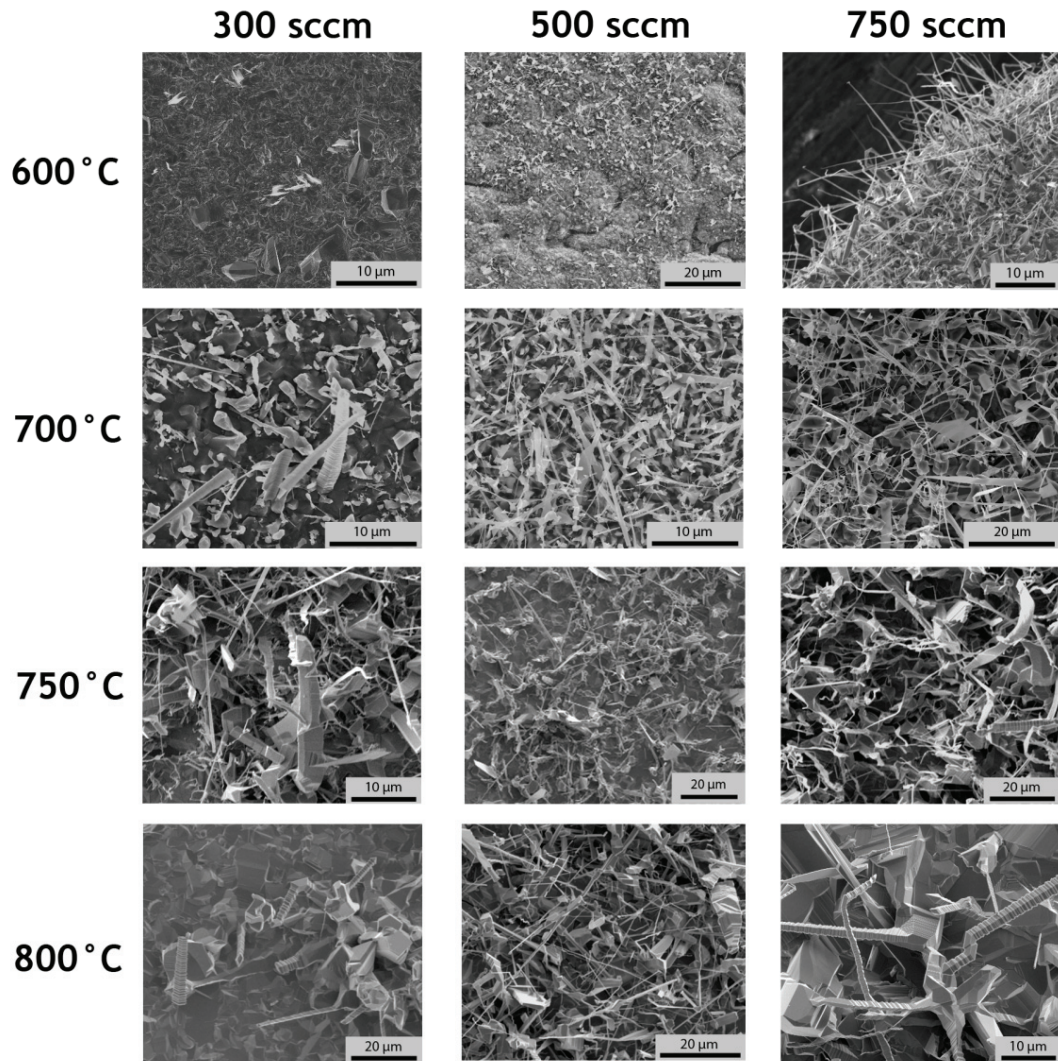


Figure 6.5: SEM micrographs showing the effects of Ar flow rate bubbled through DI water on the oxidation of CPTi foil at several temperatures.

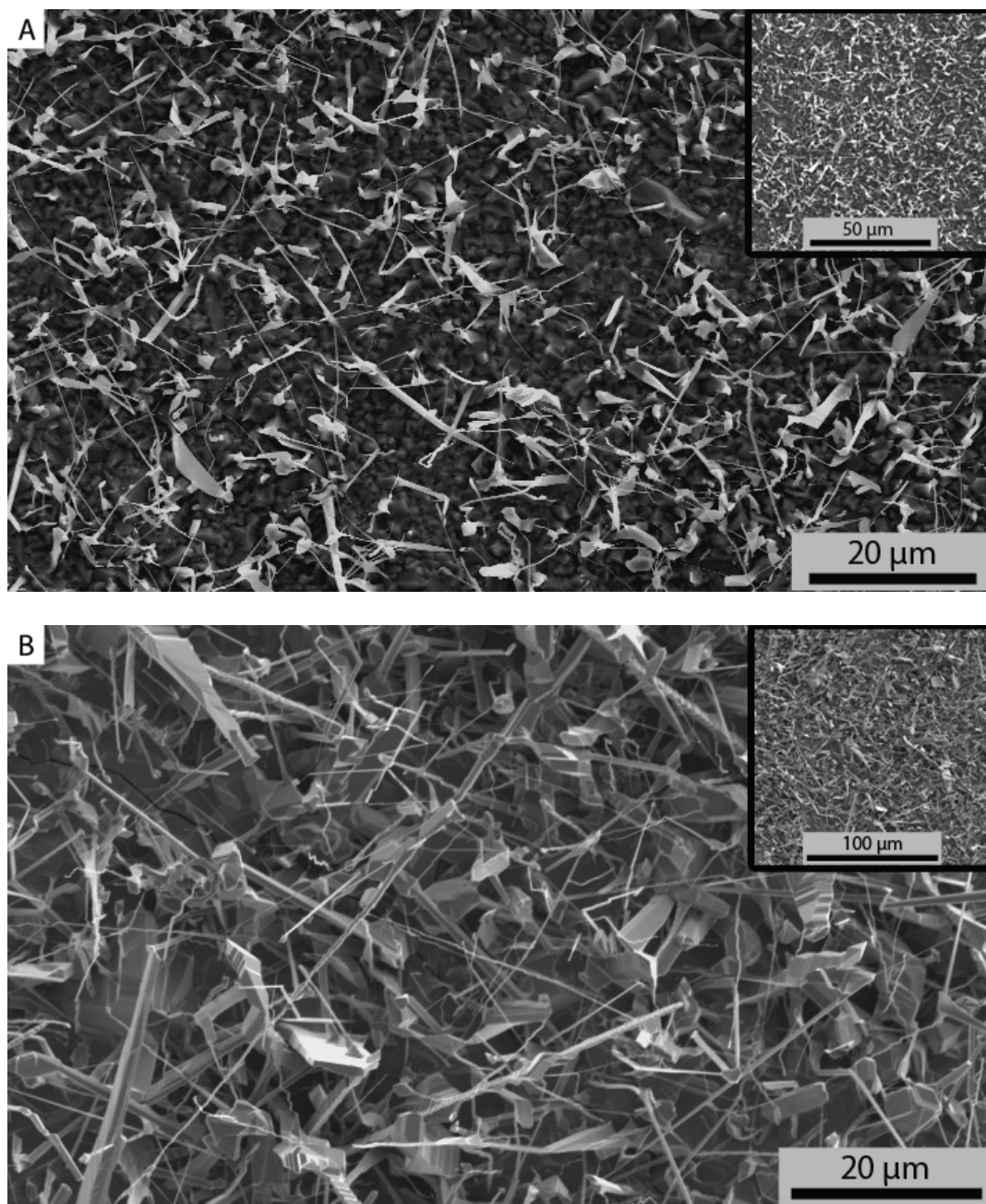
By varying the combination of oxidation temperature and the rate at which Ar is bubbled through DI water and flown into the reaction chamber one is able to tune both the relative size of the resulting nanostructures and their length. In most oxide growth processes the duration of the oxidation process typically dictates what the resulting oxide thickness would be with all other parameters held constant. This was the case in the oxidation of Ti alloys in a low oxygen environment to produce NWs as discussed in detail in Chapter 4 of this manuscript. As such, it was prudent to investigate the effect of oxidation duration on the growth of nanostructures on CPTi in wet argon. If the oxidation duration had a similar effect as was found in the Ti alloy oxidation, one would be able to select the nanostructure size based on temperature and flow rate and adjust the length by simply varying the oxidation duration.

6.4.3 Effect of Oxidation Duration

For this investigation a temperature and flow rate combination were desired such that a reasonable coverage of nanostructures was formed with nanometer scale diameters. As such, an oxidation temperature of 700°C at a flow rate of 500 sccm of wet argon was selected. Samples were oxidized for 2, 4, 16, and 20 hours under these conditions. The results can be seen in **Figure 6.6**. As the oxidation duration increased from 2 to 4 hours the average length of the NWs increased from ~17 μm to ~22 μm . The average NW length further increased to ~41 μm after 16 hours of oxidation. This trend would be expected to continue for longer oxidation durations however, the average NW length observed for the 20 hour anneal was only ~15 μm . On first consideration this seems to be a regression from the trend observed for the 2, 4, and 16 hour tests(**Fig. 6.6 A-C**)

however, after further examination of the surface morphology of the CPTi foils oxidized for 20 hours (**Fig. 6.6 D**), a 3 dimensional (3-D) network of nanostructures was observed. This network obscures the substrate from view in the SEM image making precise measurements of the NW lengths impossible. Instead, one is forced to measure the lengths from the intersection of NWs, which will be referred to as nodes hereafter, in the 3-D network. Thus, it is more appropriate to say that the average length of NWs spanning from nodule to nodule in the 3-D NW network is $\sim 15 \mu\text{m}$.

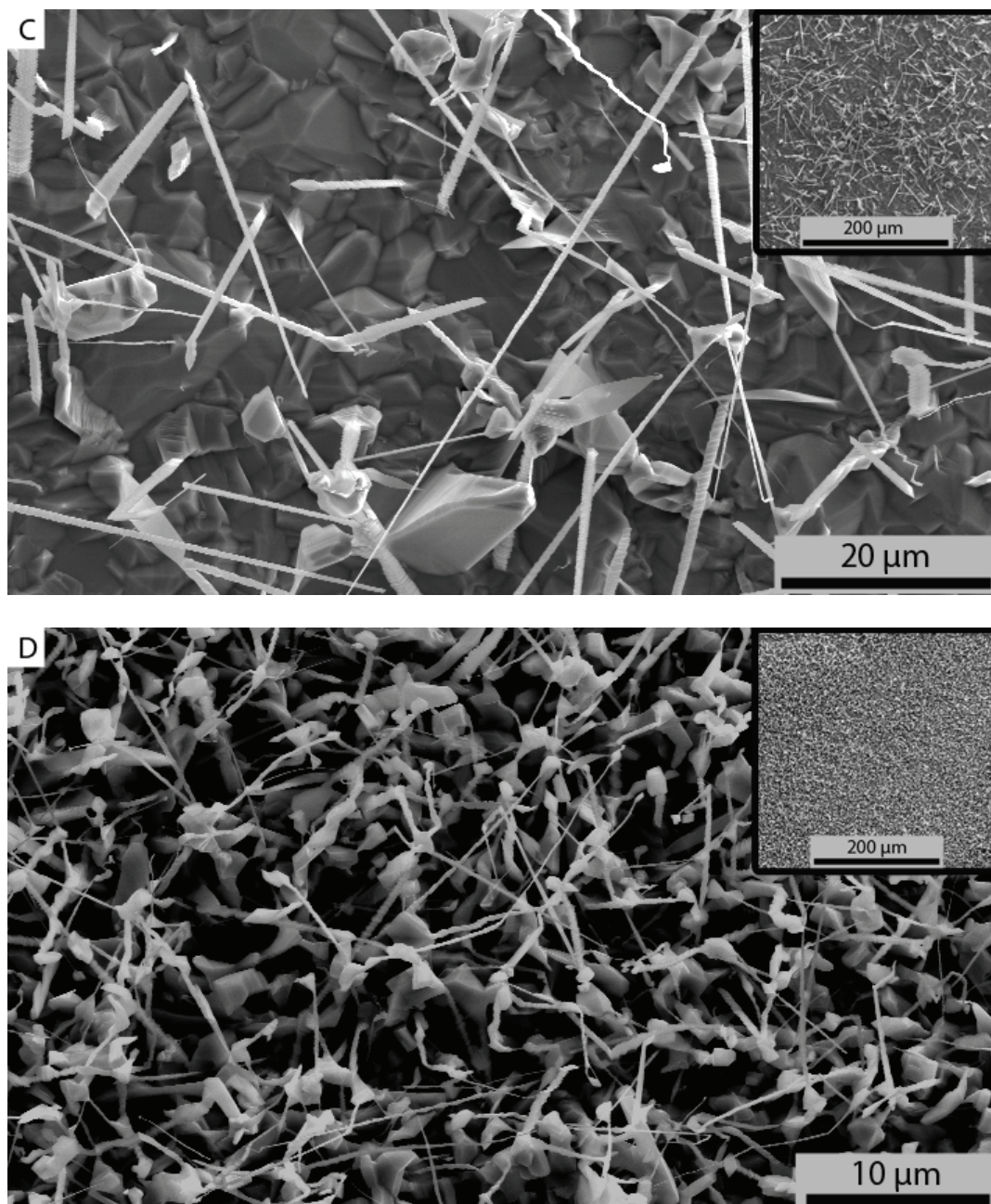
It can be surmised that an increase in oxidation duration resulted in an increase in the average length of NWs. However, as the oxidation duration increases, a corresponding increase in the likelihood of two or more NWs impinging on one another occurred. At sufficiently long oxidation times a 3-D network of nanostructures often developed. This networking phenomenon at long oxidation times has not yet been fully investigated. A comprehensive study of what conditions promote formation of the 3-D network and ways to promote or inhibit its formation should be undertaken. Additionally, shorter oxidation durations (< 2 hours) should be explored to elicit information about the early formation of the NWs. It may also be useful to observe the influence of oxidation duration on different temperature and flow rate combinations as shown in Figure 6.5. Information gained from such a study could allow for further tailoring of as-grown nanostructure morphologies to suite a given application.



continued

Figure 6.6: SEM images showing the effects of oxidation duration on nanostructure morphology for CPTi samples oxidized at 700°C under a flow rate of 500sccm of wet argon for A) 2 hours, B) 4 hours, C) 16 hours, and D) 20 hours. Insets show low magnification images of CPTi foils after oxidation.

Figure 6.6: Continued



Through the investigation of relevant oxidation parameters it was found that nanostructured oxides resulting from the oxidation of CPTi in wet argon could be tailored

by adjusting a combination of oxidation temperature, duration and gas flow rate through a DI water bath. Nanostructured oxides were produced by this process over a range of temperatures however an increase in the oxidation temperature resulted in an increase in the average size of the resulting nanostructures. The gas flow rate was found to have the greatest impact on the nanostructure morphology. This is most likely due to the impact it has on the amount of water vapor introduced during oxidation. A higher flow rate corresponds to a decrease in the humidity level in the chamber. At low flow rates (<300 sccm), a decrease in the nanostructure coverage on the CPTi samples was observed. An increase in the flow rate resulted in an increase in nanostructure coverage and length. Oxidation at high temperature and flow rate (800°C and 750 sccm) resulted in structures having diameters and lengths in the 10s and 100s of microns, respectively. The oxidation duration was shown to have a direct impact on the ultimate length of NWs formed in this process. An increase in the oxidation duration corresponded to an increase in the length of NWs. However, at extremely long oxidation times (> 20 hours), a 3-D network of nanostructures was observed. Further studies on the effect of oxidation duration are warranted.

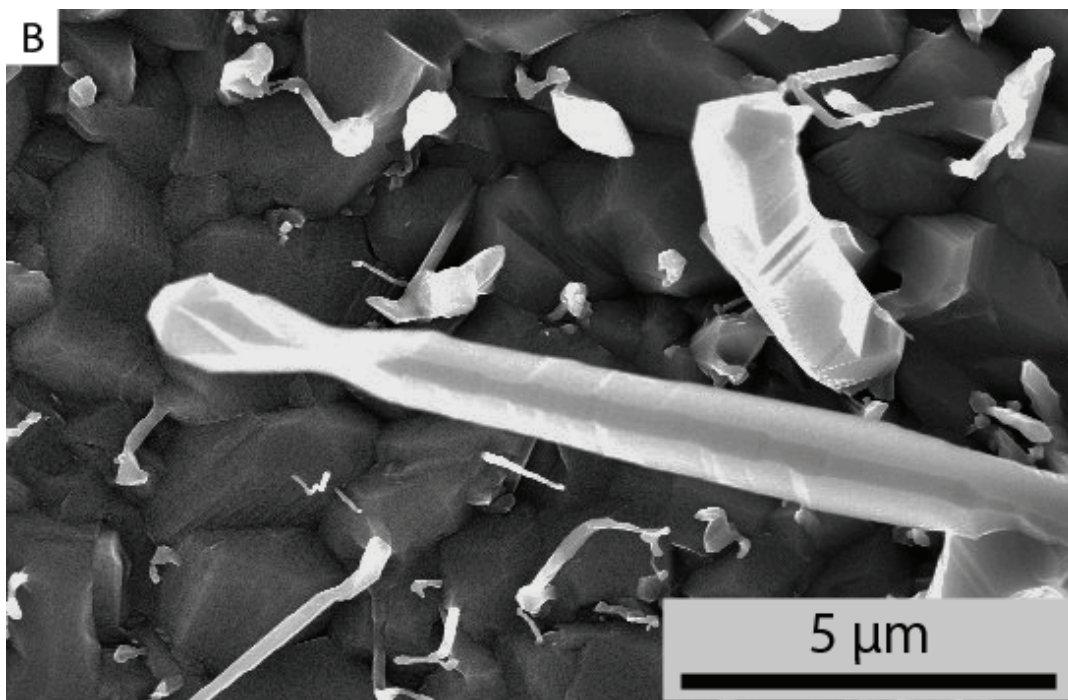
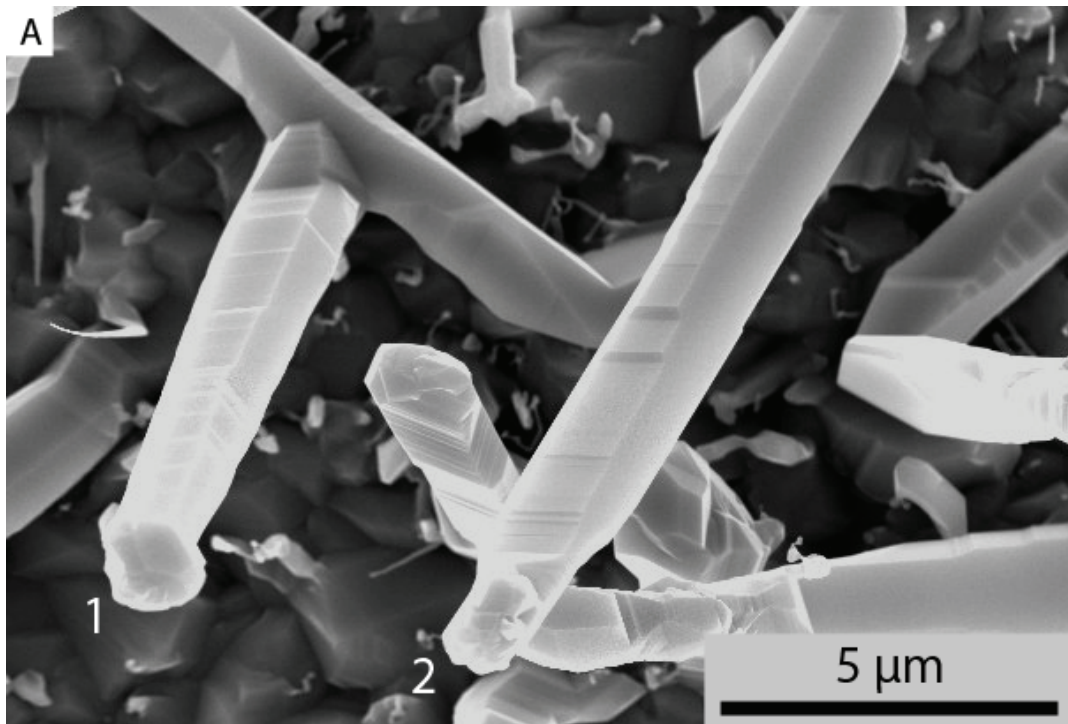
6.4.4 Variation in Oxide Morphology

It has been previously mentioned that the oxidation of CPTi in wet argon yields a wide variety of individual nanostructures. These range from smooth rod-like shapes to large ribbons. This section is devoted to highlighting some of these different nanostructures formations. The purpose of this discussion is simply to acknowledge the existence of the various nanometer and micron scale morphologies and devote some discussion to their

identifying features. Detailed structural analysis has not been completed for all structures. The analysis which has been completed will be discussed in a later section.

6.4.4.1 Rod Morphology

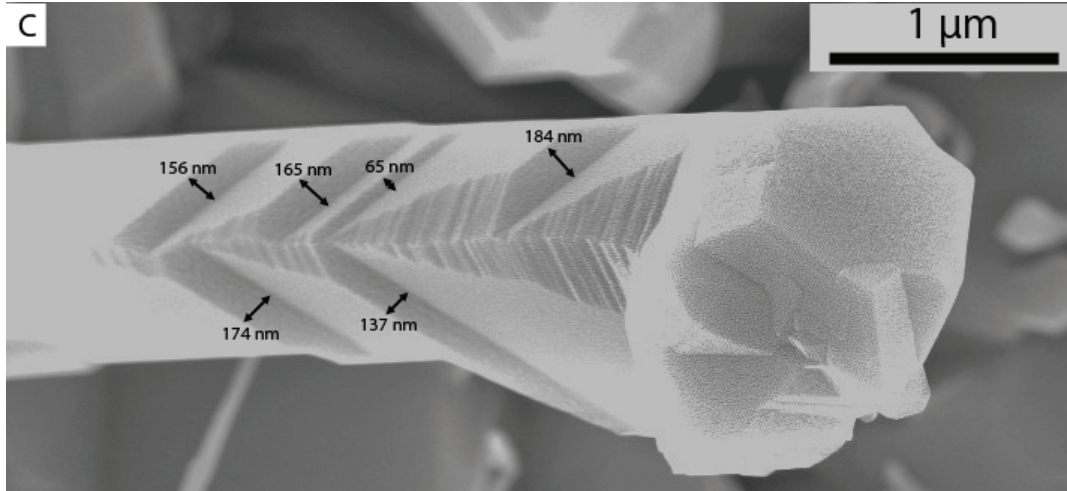
Large rod shaped structures have been observed after the oxidation of CPTi foils in wet argon as seen in **Figure 6.7**. These structures are identified by a combination of smooth and slightly stepped sides culminating in a tip having a different diameter than the trunk of the rod. The tips can either be smaller or larger in diameter than the trunk as shown by the rods labeled 1 and 2, respectively in **Figure 6.7 A**. These rods are typically 2 - 4 μm in diameter and 5 – 20 μm in length. The structures have been observed growing out from the substrate and branching out from other structures (**Fig. 6.7 A**). A thinning of the rod between the trunk and the tip has also been observed (**Fig. 6.7 B**). **Figure 6.7 C** shows a high magnification view of this necking and the tip of the rod. The neck is made up of several sharp, well faceted steps where each step reduces the rod's diameter by 65 – 185 nm. The rod's tip also exhibits a stepped appearance however it appears to have a spiraled step pattern. Additionally, the diameter of the tip of the rod at its widest point is almost twice that of the trunk below the neck. To date this structure has not been characterized by any methods other than SEM and bulk XRD analysis. Further characterization of the rods probing specifically for phase identification and the crystallographic orientation of the different faceted faces may prove interesting and would be of scientific merit.



continued

Figure 6.7: SEM images of rod shaped structures formed from the oxidation of CPTi foils at 700°C for 4 hours at a wet argon flow rate of 750scm.

Figure 6.7: Continued



6.4.4.2 *Plateau Morphology*

In addition to the large rods, flat plateau like structures were observed via SEM growing out from the surface of the Ti foils after oxidation. These structures, as seen in **Figure 6.8**, were several microns in diameter/length and were typically accompanied by very large blade like structures. The plateau structure shown in **Figure 6.8 B** resembles the sole of a shoe due to multiple faceted faces on its surface. Of the oxide structures discussed in this section, the plateau type was the least commonly observed structure being found on only a limited sampling of oxidized CPTi foils. Careful observation of future oxide samples produced by this process should be made to look for more occurrences of this structure. Additionally, further analysis of the existing samples may yield more information as to the orientation and makeup of these structures.

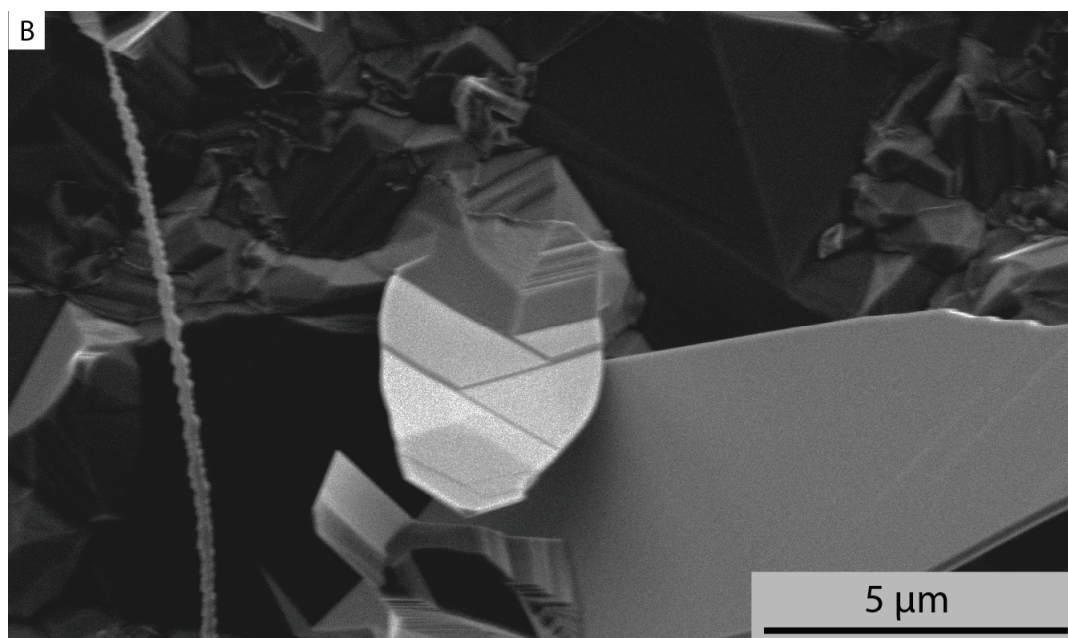
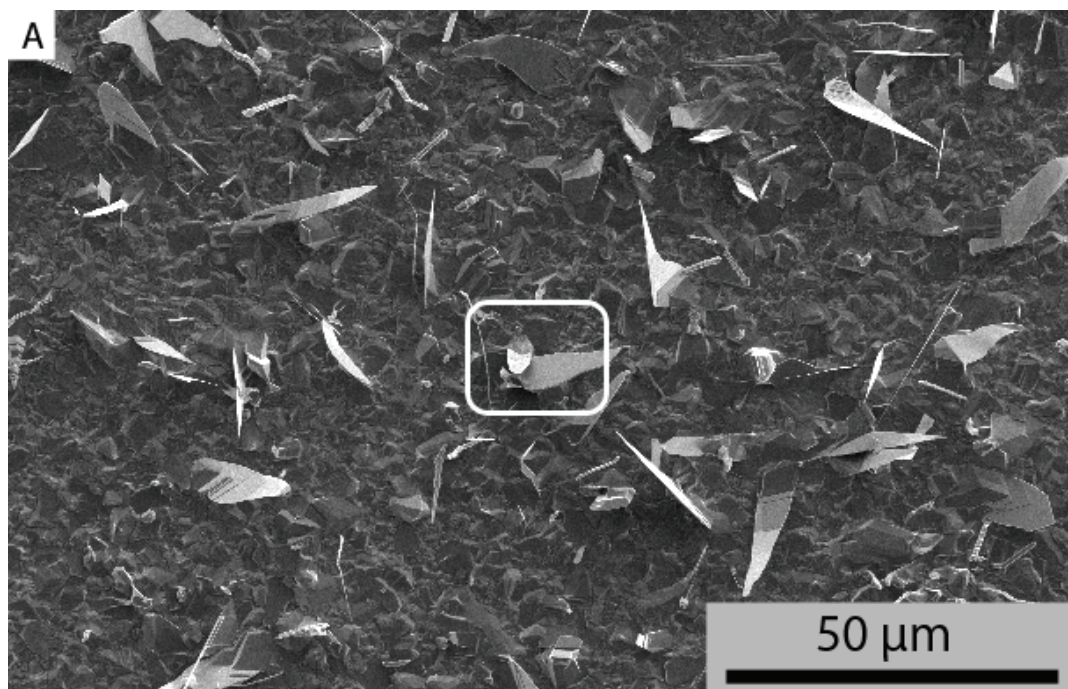
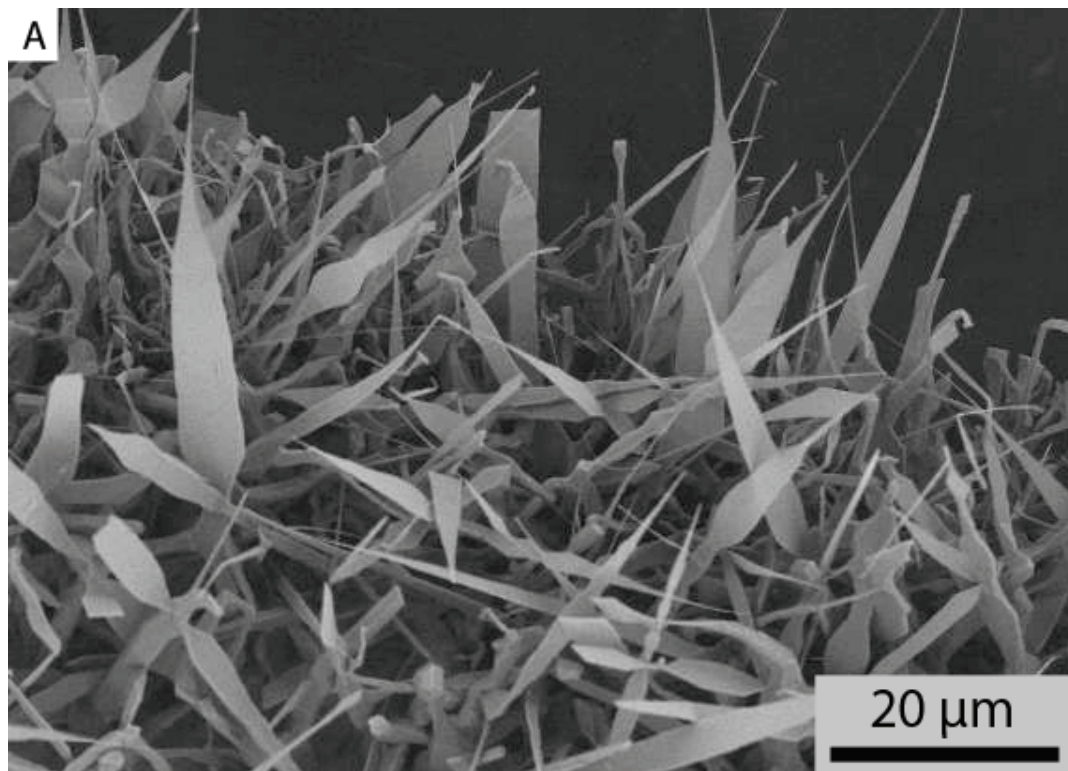


Figure 6.8: SEM micrographs of “shoe-sole” type oxide morphology grown on CPTi foil.

6.4.4.3 *Ribbon Morphology*

Another interesting structure formed by the oxidation of CPTi foils in wet argon is observed in the micrographs of **Figure 6.9** and can be described as ribbons. These structures are typically 10s of microns in length and 1 – 10 microns in one of the lateral dimension. The other dimension is much smaller usually only in the hundreds of nanometers as noted in **Figure 6.9 B**. The shape of these structures is less uniform along their lengths compared to the rods previously discussed and strongly resembles ribbons. They tend to be wider near the base tapering towards a point at the tip (**Fig. 6.9 A-C**). This thin tip can easily be 10s of microns in length and may be best described as a whisker or wire. This form is often found in groupings of many ribbons having similar dimensions. **Figure 6.9 B** shows the most common morphology for this structure; a fairly thin body widening slightly towards the tip before thinning again forming a diamond shape at which point the tip normally narrows significantly while growing several more micrometers (note the ribbons in **Fig. 6.9 A**). The ribbon isolated in **Figure 6.9 B** has an interesting feature in that once the tip narrows it turns back on itself and continues to grow at an acute angle to the trunk of the ribbon. A thickening of the elongated tip is also observed in this ribbon. Ribbons have also been observed where the base of the ribbon, where it emerges from the substrate surface, is 2 – 10 microns wide and decreases relatively uniformly over its entire length forming a sharp point at its tip (**Fig. 6.9 C**). Occasionally, the ribbon structures are observed growing in clusters as shown in **Figure 6.9 D** where several ribbons are growing in the same orientation out from the surface of a grain while another ribbon forms almost perpendicular to the group. This later form has been seldom observed and is significantly less common than the structures observed in

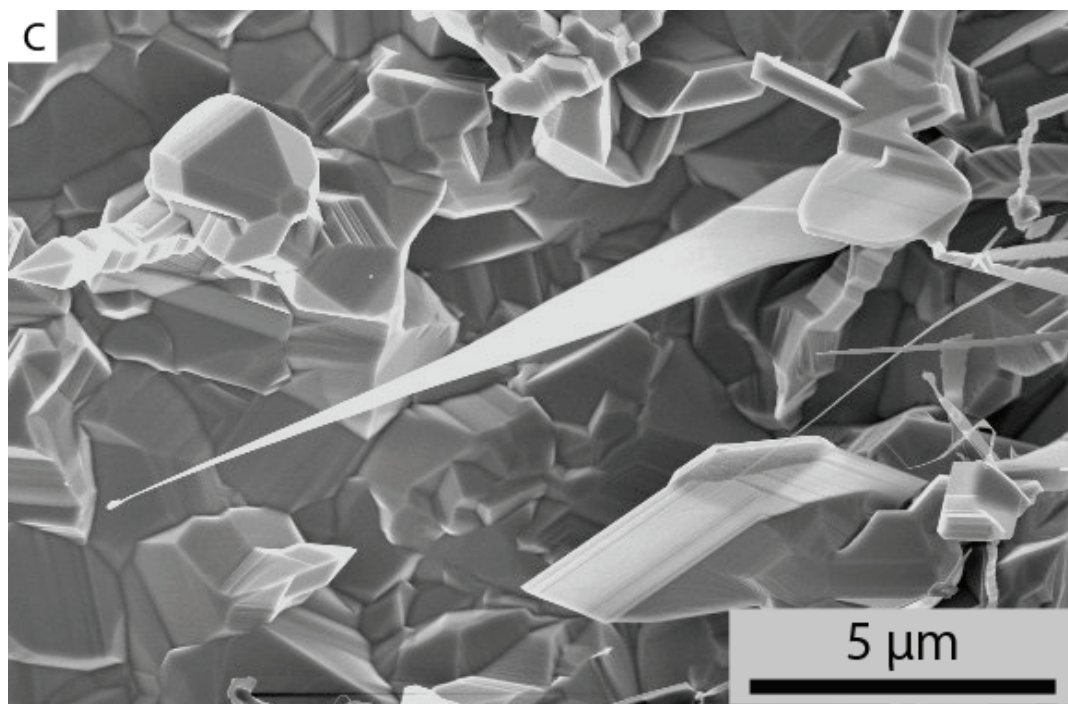
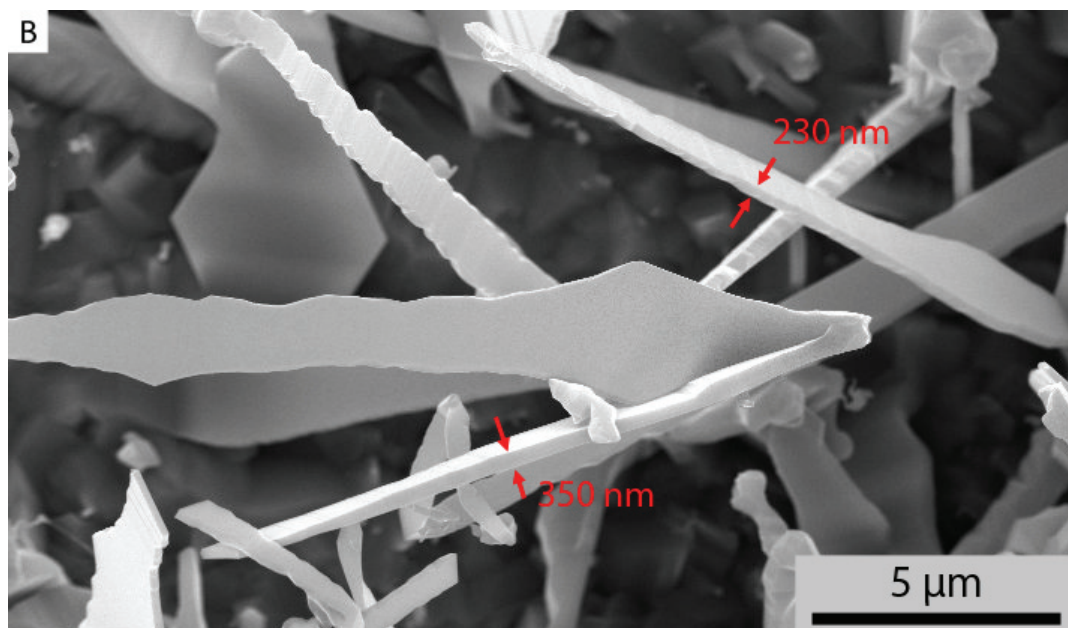
Figure 6.9 A-C. The ribbons have been characterized via TEM analysis the results of which include structure determination and a discussion of the growth direction. These results will be discussed in a later section.



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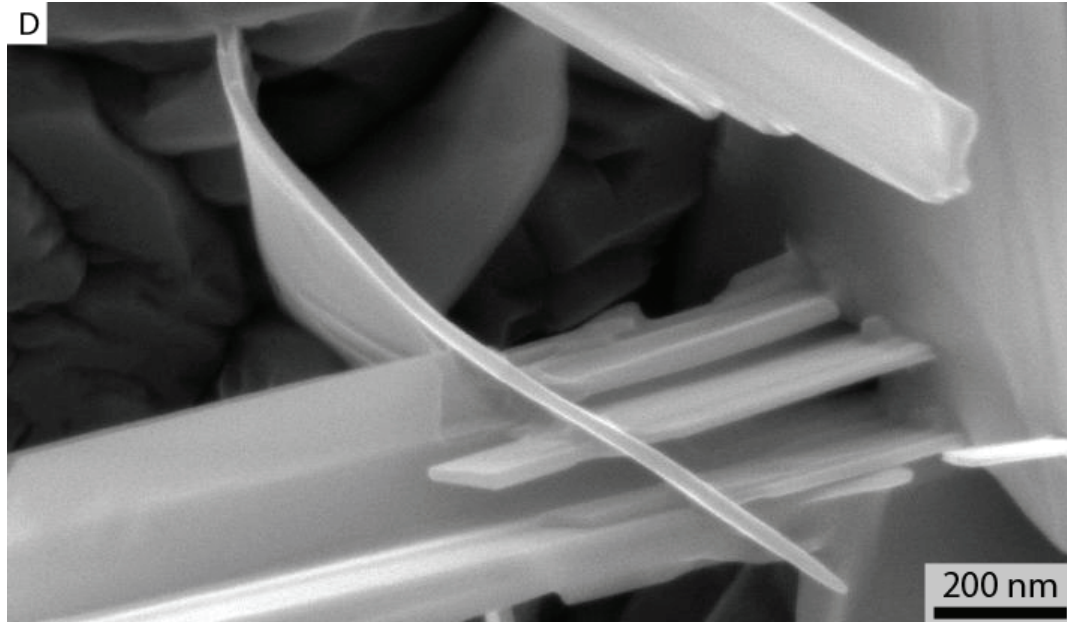
Figure 6.9: SEM micrographs showing various ribbon morphologies produced by oxidation of CPTi foil in wet argon.

Figure 6.9: Continued



continued

Figure 6.9: Continued



6.4.4.4 *Stacked Nanowire Morphology*

The most prevalent structure to form during the oxidation of CPTi at elevated temperature in wet argon was wires exhibiting a faceted surface appearing to be made up of many square or rectangular plates stacked atop one another. These structures were observed resulting from all oxidation parameters tested. There are two distinct morphologies observed for the stacked NWs as presented in **Figure 6.10**. The first, box number 1 in **Figure 6.10 A**, is a long wire with a fairly constant average diameter along its length culminating in a sharp point at its tip. The body or trunk of the wire is made up of what appear to be many parts at slight alternating angles to one another such that they offset the previous segments angle to form an overall straight structure. This morphology has been observed with lengths varying from 100s of nanometers up to 10s of microns.

The second distinct morphology is highlighted in box 2 of **Figure 6.10 A**. This wire formation is also of a stacked type structure but there is no apparent angle offset between adjacent layers. Instead, alternating layers have different diameters such that space appears to exist between every other layer as seen in **Figure 6.10 B**.

While there are two variations observed for the appearance of the stacked structures there are a total of four tip shapes that have been identified for these structures. Representative micrographs of these variations are shown in **Figure 6.11**. Prior to this discussion it should be noted that three of the four micrographs shown in **Figure 6.11** show large structures that are not nanometers in scale. These four different tip shapes have been observed in both the nanometer and micrometer regimes though the clearest images are seen in the larger structures. The four tip variations can be summarized as follows; A) small rounded tips aligned with the wire's axis, B) flat tips with slightly larger diameters than the trunk of the wires that end abruptly, C) faceted heads that bend back towards the wire trunk ending in a point, and D) highly faceted tips that come to a sharp point.

Comparing tips C and D, their appearance is quite similar with the only variation between the two being the angle that C makes with the wire trunk. These different tips are quite interesting and may be suitable to specific applications such as electron and x-ray emissions.[37, 186] Further studies into the cause(s) for one tip variation over another are warranted. The application of these different structures is also fertile ground for further investigation.

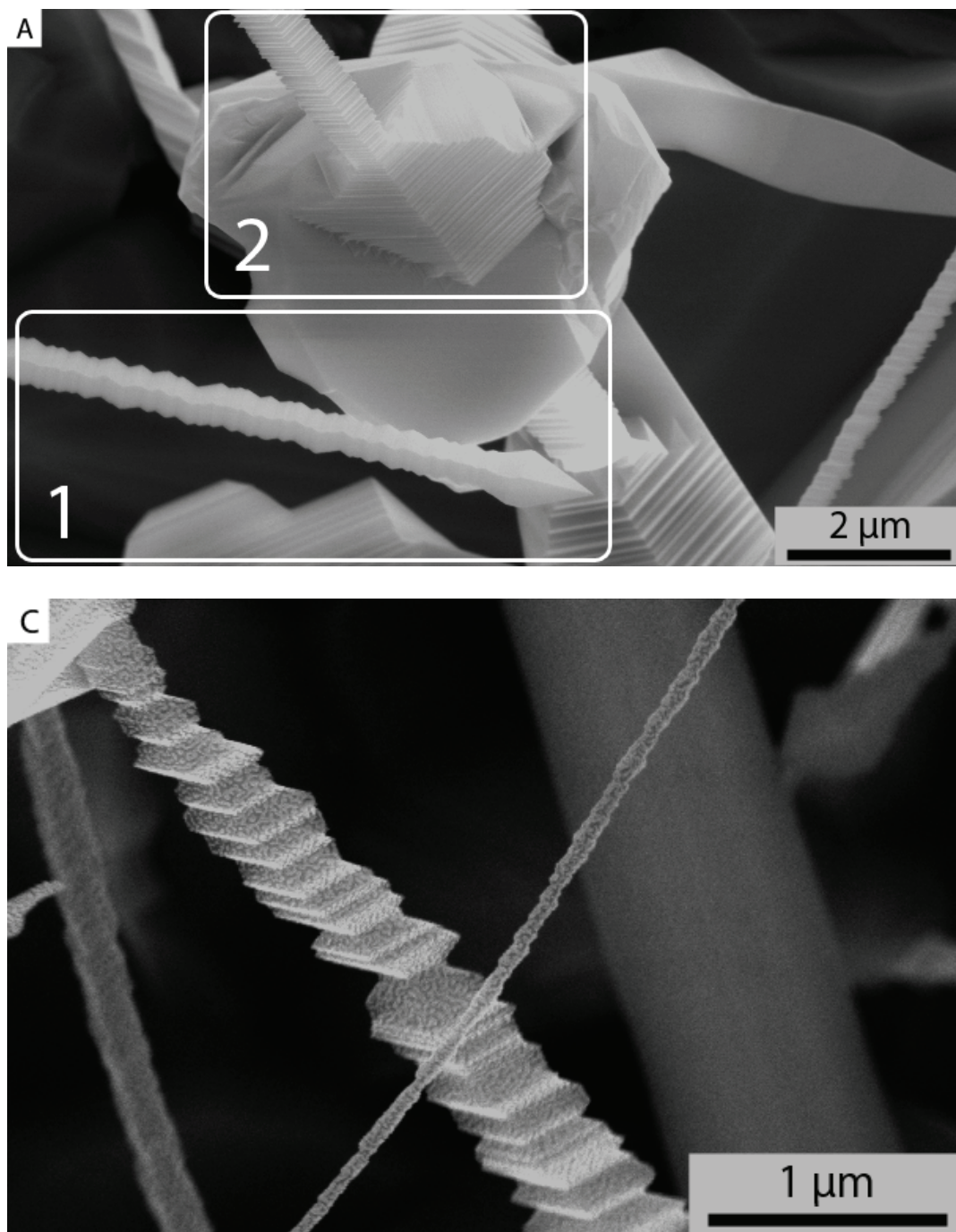


Figure 6.10: SEM micrographs showing A) two distinct morphologies observed for the stacked NWs. B) Individual stacked layers have been observed in these structures.

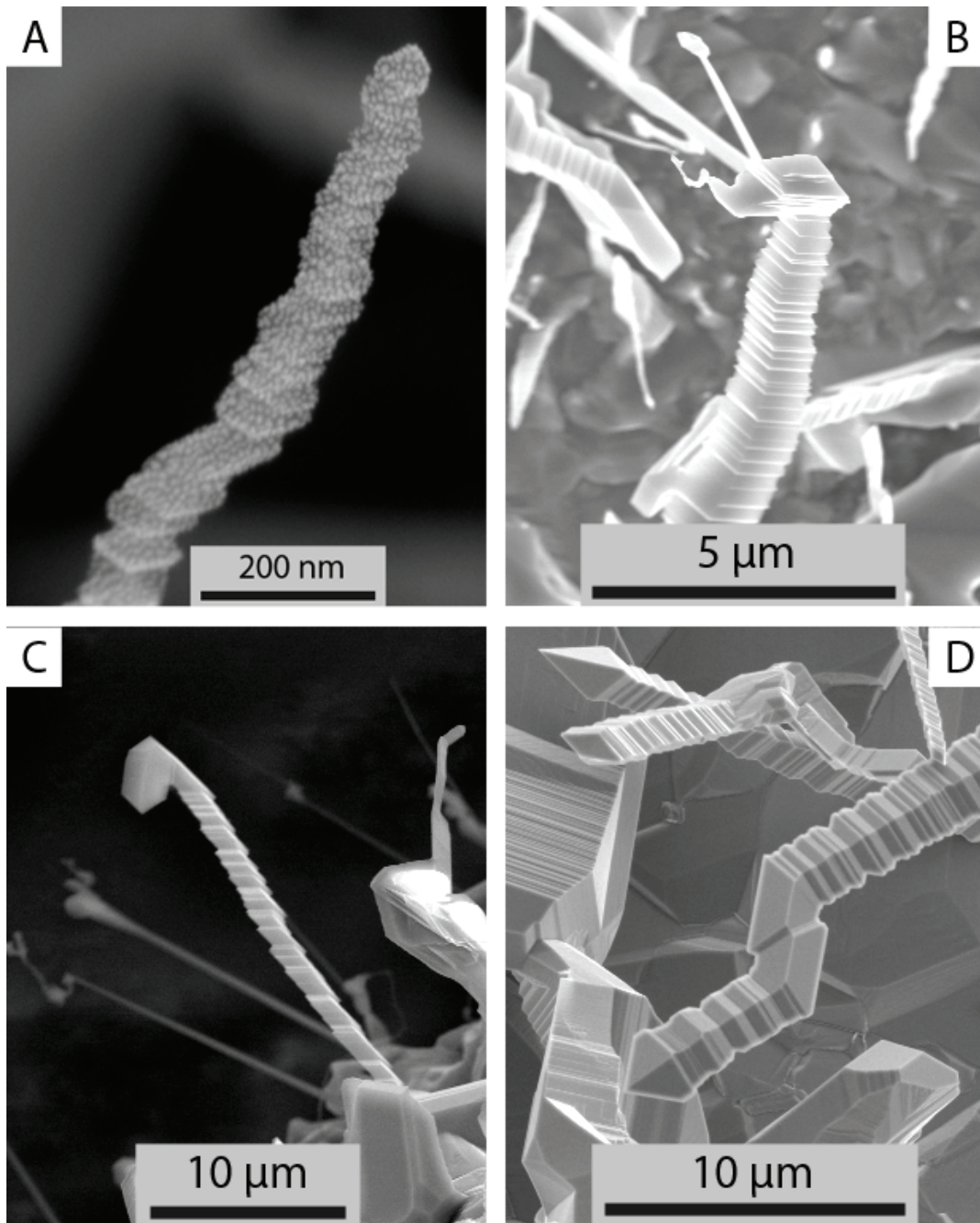


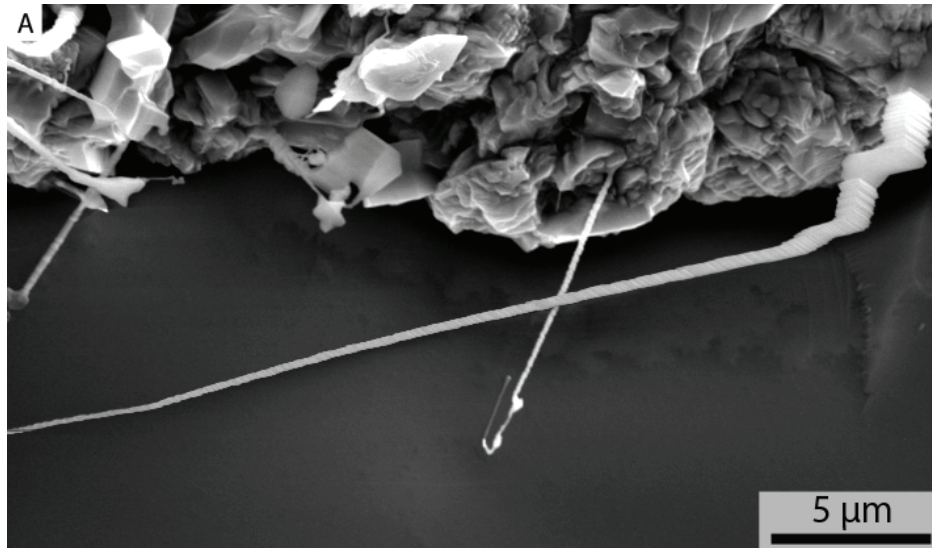
Figure 6.11: SEM images showing different tip morphologies for the stacked type structures.

6.4.4.5 *Morphological Oddities*

Most of the structures in the preceding discussion have been shown growing in a relatively straight manner. That is, there is very little variation in the growth direction for the structure. This is not always the case. Quite often this is the exception rather than the rule for a given oxidized sample. More typically the structures take extreme turns while growing resulting in a structure that is not straight. This behavior has previously been shown (**Figures 6.5, 6.9 B, and 6.11 D**). The change in growth direction has been observed early in the growth process with the new growth direction being maintained for the duration of the oxide formation as shown in **Figure 6.12 A**. However, the growth direction may also change several times during the growth cycle of the structure resulting in a zigzag formation as observed in **Figure 6.12 B**. In both of these cases, the resulting wires had a net growth direction that corresponded to an elongation of the structure. A complete change in the growth direction equal to a 180° turn has also been observed. This type of growth behavior can be observed in **Figure 6.12 C and D**.

Looking first at **Figure 6.12 C**, a stacked type NW can be seen growing vertically from the sample surface for some time before forming a flat plateau. After which, it appears to grow back down towards the sample surface. An alternate explanation for the observed structure is that two stacked type NWs were growing side by side, parallel to one another, from the surface of the substrate. Towards the end of the oxide growth a neck formed between the two adjacent wires resulting in the smooth plateau. Both explanations for the resulting structure are plausible but it would require direct observation during formation to determine which, if either, scenario were in fact true. The structure observed in **Figure 6.12 D** is not so ambiguous in terms of growth from one or two structures. A loop of wire

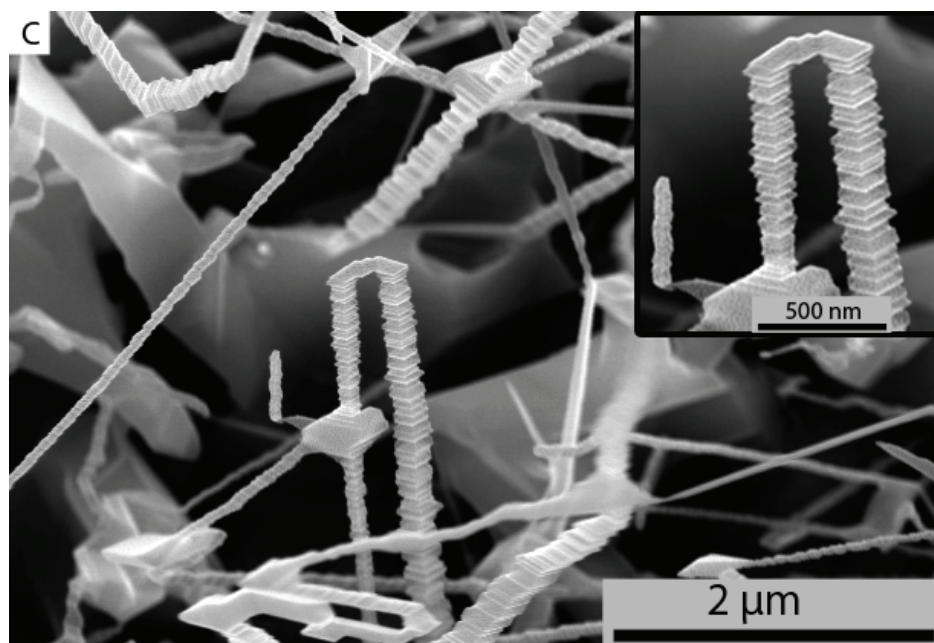
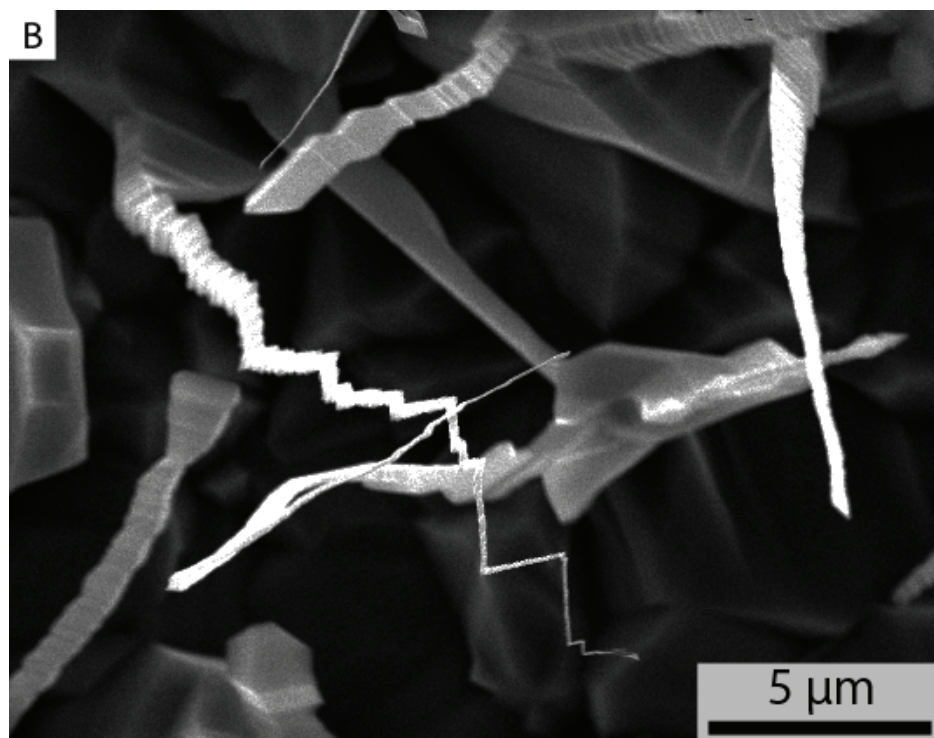
can clearly be observed originating from a single wire. While parts of the wire show stacked type morphology, the portions involved in the loop are smooth and appear to be continuous along their lengths.



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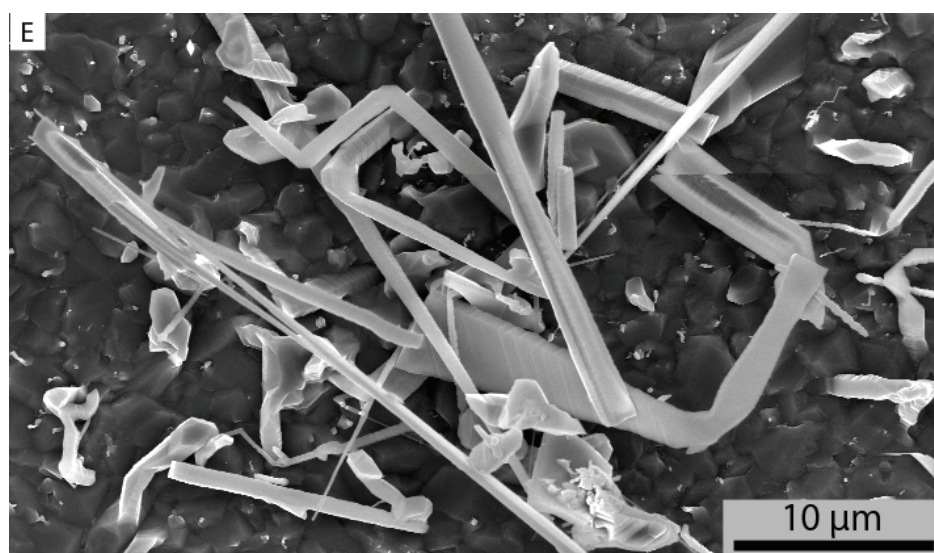
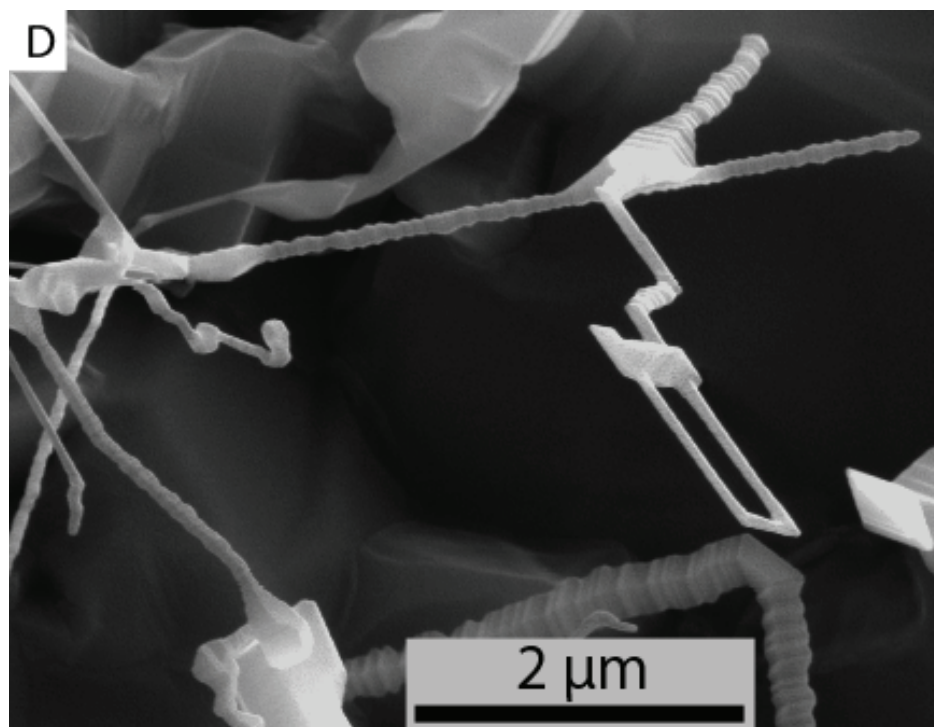
Figure 6.12: SEM images of high angle bends forming in as-grown oxide structures. Inset in C) shows high magnification image of 180° bend.

Figure 6.12: Continued



continued

Figure 6.12: Continued



The previous examples of change in growth direction have demonstrated this behavior in the stacked type oxide morphology however, this behavior has also been observed in the

other structures outlined throughout this section. For example, **Figure 6.12 E** demonstrates this behavior in the micrometer sized rods. Several very sharp ($\sim 90^\circ$) bends can be observed in multiple rods. This behavior has also been observed in the ribbon morphologies as previously shown in **Figure 6.9 B**. Since the behavior is not limited to only one or two of the observed oxide morphologies produced by the oxidation of CPTi in wet argon it may be concluded that it is a feature of the oxidation process independent of morphology. This conclusion should be tempered with the realization that the turning behavior is most commonly seen in the stacked NWs and that some of the morphologies may be more prone to this behavior than others. Further studies are required to obtain a better understanding of the root cause for this behavior and to determine what, if any, defects may be involved.

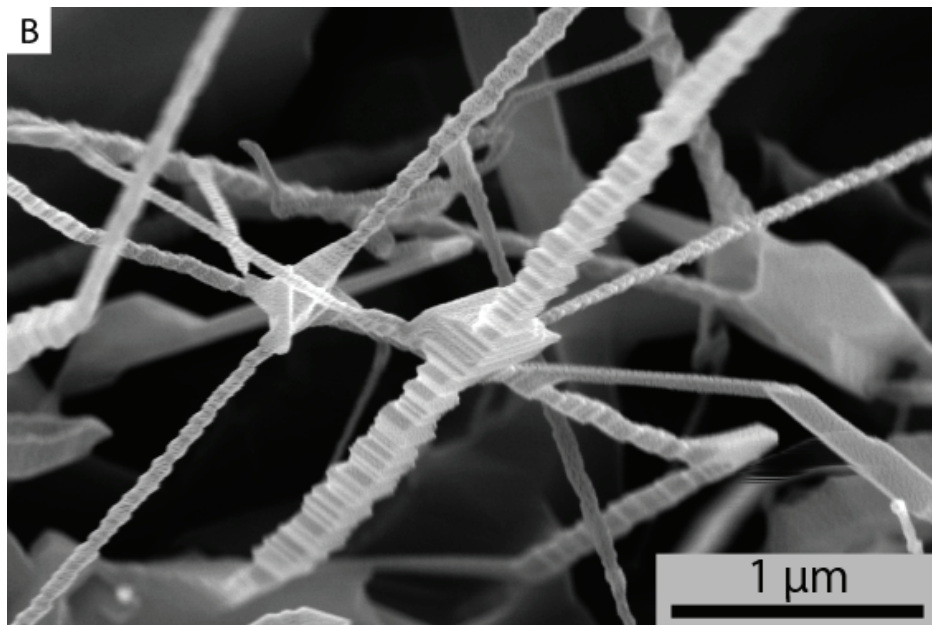
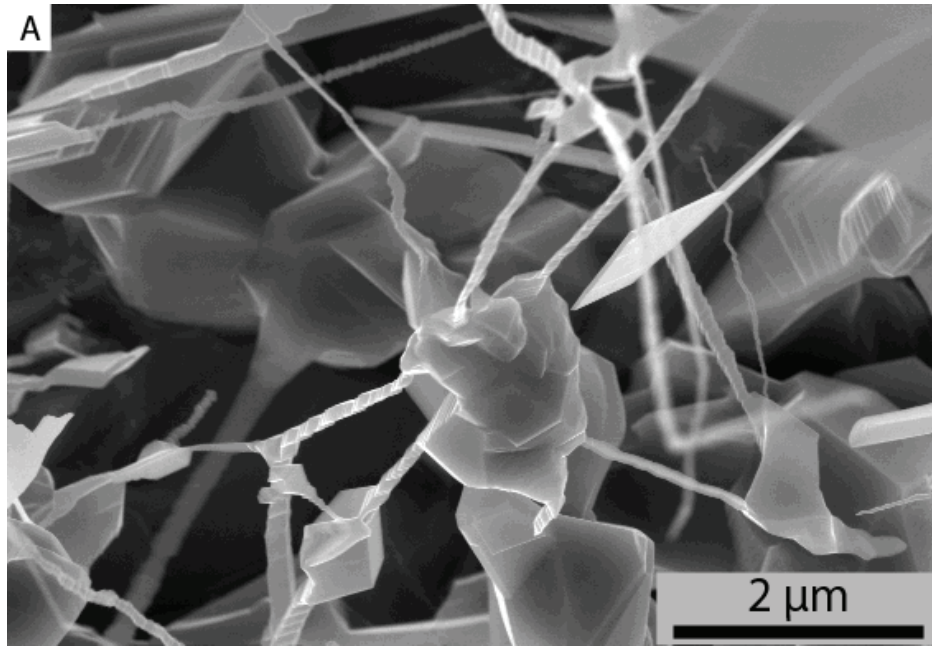
6.4.4.6 *Node Formation*

A sharp change in direction is not the only strange behavior observed for structures grown in wet argon. Another, perhaps more interesting oxidation behavior observed in these trials was the joining of one or more NW to form a node or network as observed in **Figure 6.13**. This behavior was most commonly observed in samples oxidized at high Ar flow rates (750 sccm). In these samples the structures grew such that a 3-D network was formed by multiple NWs growing into one another as observed in **Figure 6.13 A**. In this image, five distinct NWs can be observed emerging from a single node. The NWs are not all emanating from the same point but rather appear to originate at multiple angles and heights. The node is large and globular having no regular shape. This is not always the case for nodes. They have also been observed with extremely regular faceted shapes (**Fig.**

6.13 B and **C**). It is not absolutely clear whether the node forms due to the intersection of two or more wires during growth or if it is the source for these wires. **Figure 6.13 C** is an image of a node where four wires are intersecting in space. It is not apparent if any of these wires originated from the node but it appears that the left most wire is just starting to come in contact with the node. This would indicate that the node and at least the left most wire formed independently. In contrast, **Figure 6.13 D** shows a node structure that has clearly formed from one initial wire growing vertically from the substrate. At some point in the growth process the conditions were favorable for a node to form from which two wires started to grow perpendicular to the original wire. The parent wire also appears to continue growing in its original growth direction forming a second node a few hundred nanometers later. Again, two more NWs can be seen growing outward from this second node. This image would indicate that the node forms independent from an intersection of two or more wires. This is further supported by **Figure 6.13 E** where a node has formed from a single wire and appears to have “sprouted” two additional wires the left most of which looks as if it is in its infancy.

Numerous oxide structures have been observed resulting from the oxidation of CPTi foils at elevated temperatures in wet argon. Most of these structures occur at multiple size scales and under several different oxidation conditions. For example, the stacked wire morphology shown in **Figure 6.10** has been observed in every combination of oxidation parameters tested. The size of the structures varies but the identifying features are present in each case. Multiple tip formations have also been observed but these appear to simply be variations of the same tip morphology. Some questions remain unanswered: *What*

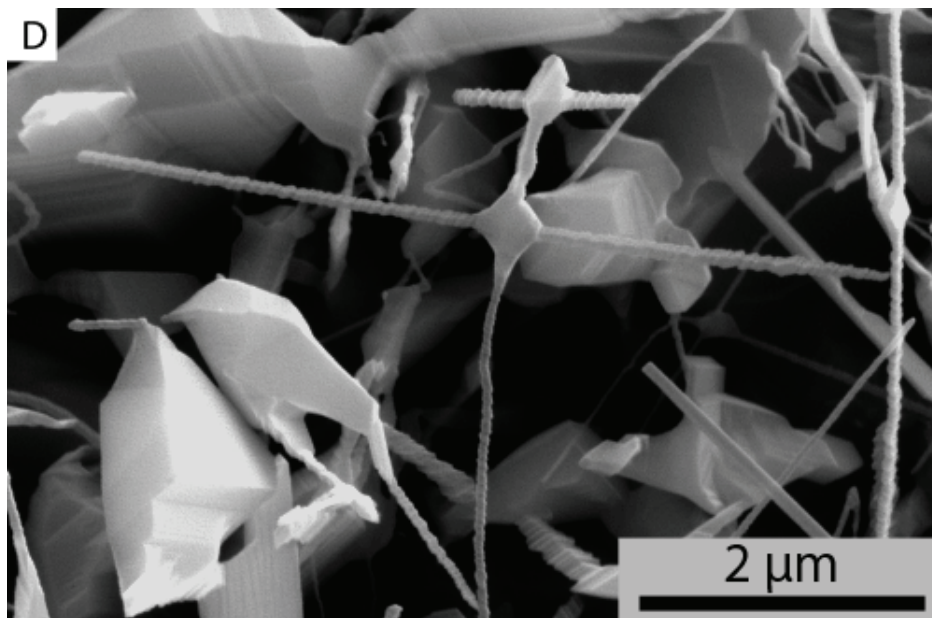
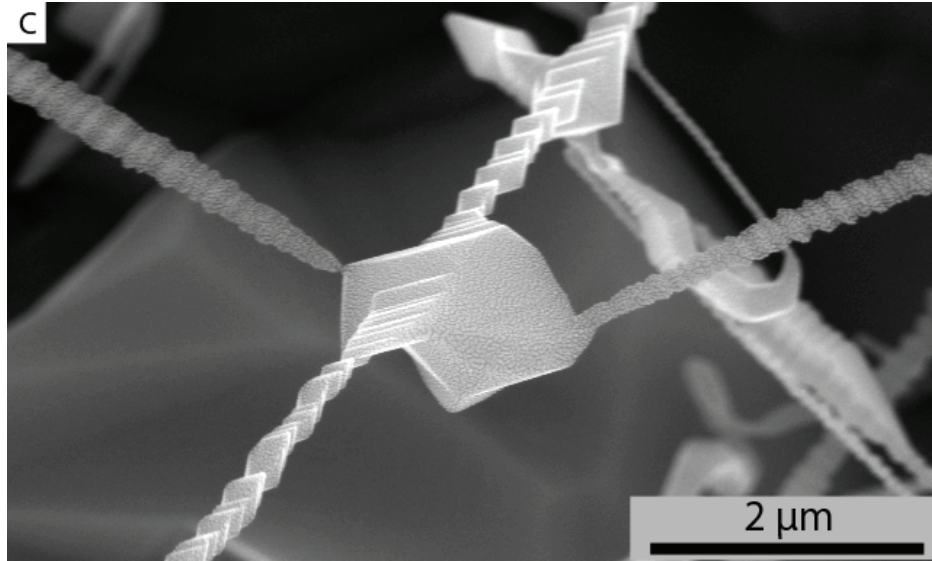
causes the different oxide structures to form? Why would one structure preferentially grow over another? Several structures of different type have been observed growing in close proximity to one another. Is the gas environment in that specific region significantly different from another? Is it some local variation in the substrate that ultimately dictates which structure will grow? High angle turns in the formation of the structures have also been observed. This is very interesting from a crystal growth point of view. What would cause such a drastic change in growth direction for a crystal? What defects could be present to allow for this type of behavior? The node formation is also of specific interest. Why and under what conditions do these nodes form? Do they more often form from an individual structure or from the intersection of two or more structures growing into one another? While these structures are extremely interesting, they raise many questions which have not been answered.



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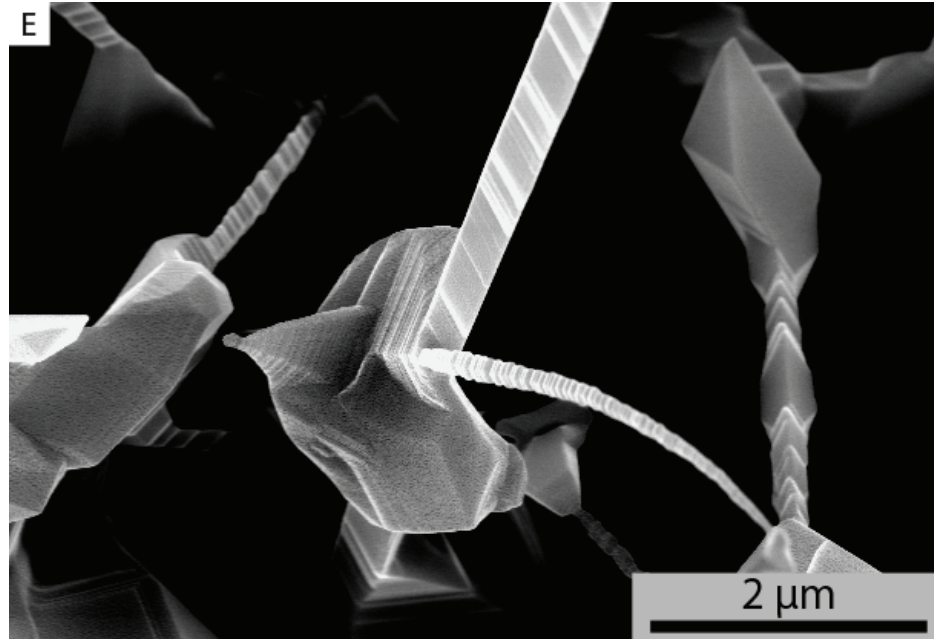
Figure 6.13: SEM images showing various node formations produced during the oxidation of CPTi in wet argon.

Figure 6.13: Continued



continued

Figure 6.13: Continued



6.5 Nanostructured Growth on Titanium TEM Grids

Throughout the previous discussion all oxidation experiments were conducted using CPTi foils. While this is an ideal platform for testing a variety of parameters and observing the as-grown structures it presents certain challenges if one is interested in characterizing individual NWs. One specific challenge encountered pertains to the characterization of the oxide structures via TEM. While the majority of the structures are electron transparent and therefore ideal for characterization by TEM, they are attached to a substrate which is not electron transparent. Often, NW TEM samples are prepared by removing the NWs from their substrate by either scraping or ultrasonication however this approach has an inherent problem. Once removed from the substrate, it becomes exceedingly difficult to identify which end of a NW was originally attached to the

substrate and which end was exposed to the oxidation environment. It would be ideal if the NWs could be grown in such a way as to allow the sample to be directly placed in a TEM without the need for removal of individual NWs. Chen *et. al.* reported the successful growth of CuO NWs on copper substrates in air.[14] High aspect ratio CuO nanostructures were grown on Cu foils at elevated temperatures in laboratory air. Jiang *et. al.* successfully translated this growth technique to standard Cu TEM grids.[16] This prompted an investigation into the feasibility of the direct oxidation of commercially available CPTi TEM grids. 300-mesh Ti TEM grids were oxidized at 700°C for 4 hours under 500 sccm flow of wet argon.

First attempts at oxidation yielded poor results for NW formation. In this early work, TEM grids were laid on pieces of polished alumina for support during oxidation and to facilitate insertion and retrieval from the reaction chamber. To characterize the grid surface via SEM, the grids were transferred onto double sided copper tape and adhered to a standard aluminum SEM stub. Initial results can be observed in **Figure 6.15**. After oxidation in wet argon the grids were extremely brittle and broke into several pieces upon contact. The oxidized grids contained very little nanostructured growth (left inset in **Fig. 6.14 B**) with no growth occurring in the holes of the grid (right inset in **Fig. 6.14 B**) as would be desired for TEM studies. To increase the likelihood of NW growth in the holes, the grids were placed vertically into the reaction chamber. This was achieved by cutting a shallow recess (~1 mm) into a piece of bulk Ti and placing the Ti TEM grid vertically into this recess. Changing the grid orientation during oxidation dramatically increased the nanostructured growth resulting in a large number of NWs growing radially into the grid

holes as seen in **Figure 6.15**. The successful formation of NWs in the holes of TEM grids allowed for direct image and evaluation of the as-grown NWs by TEM (**Fig. 6.15 C**).

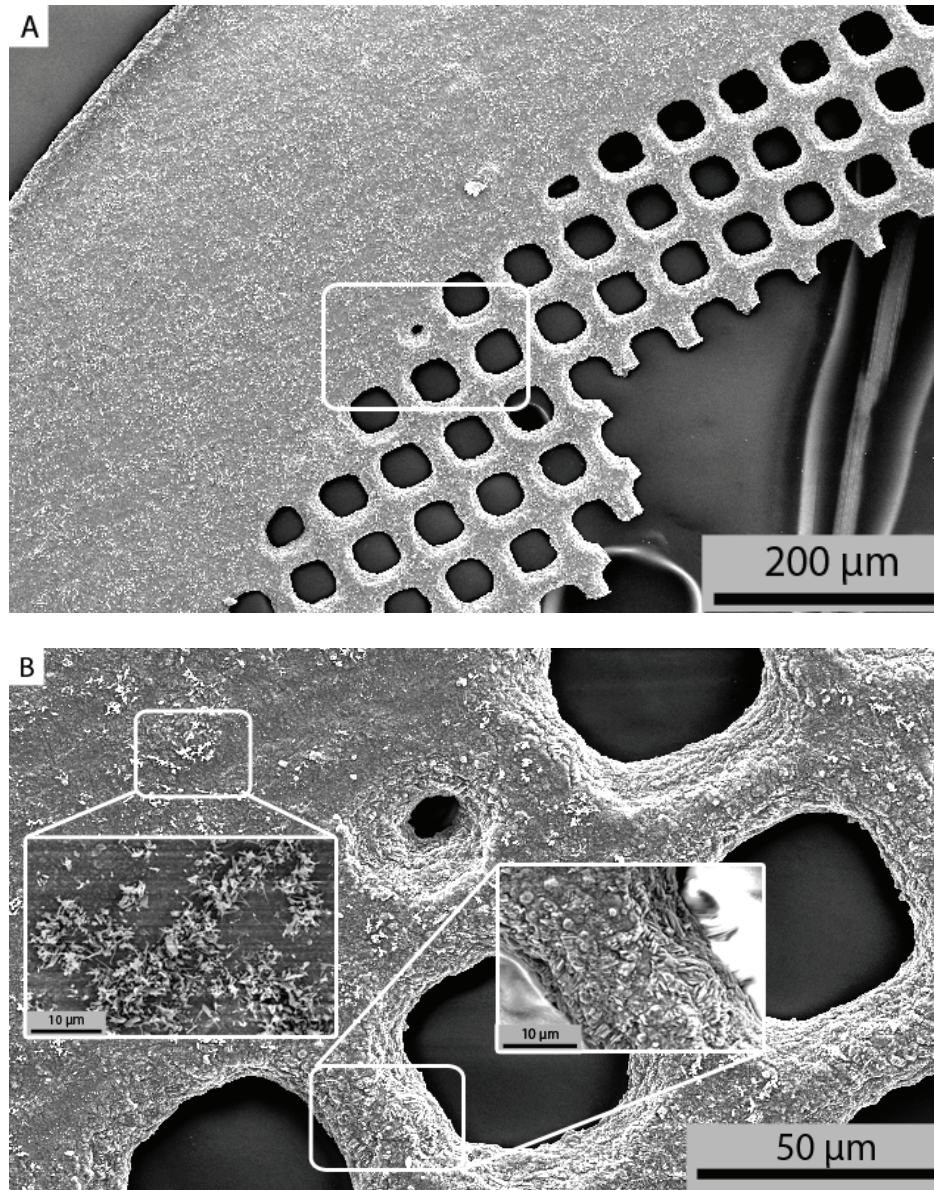
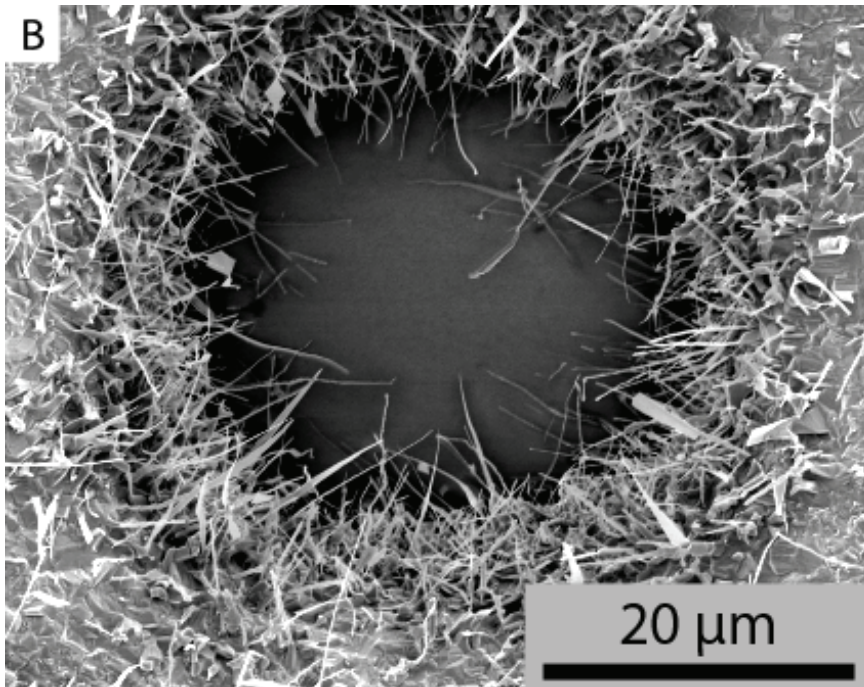
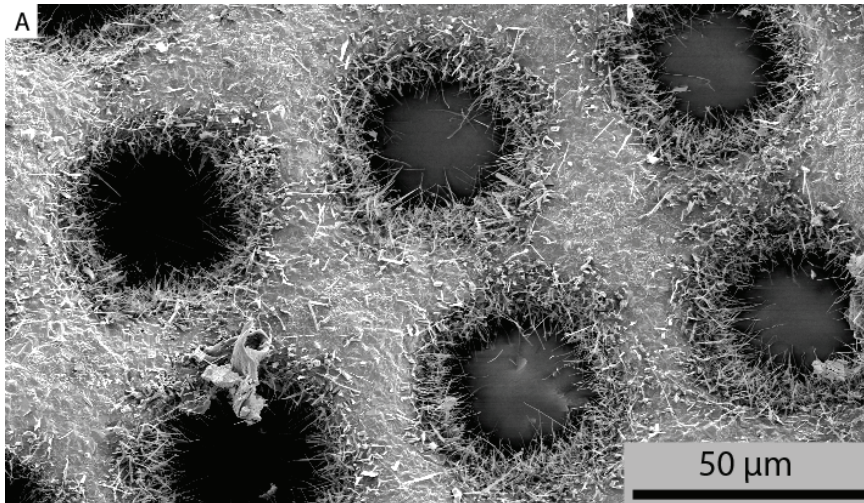


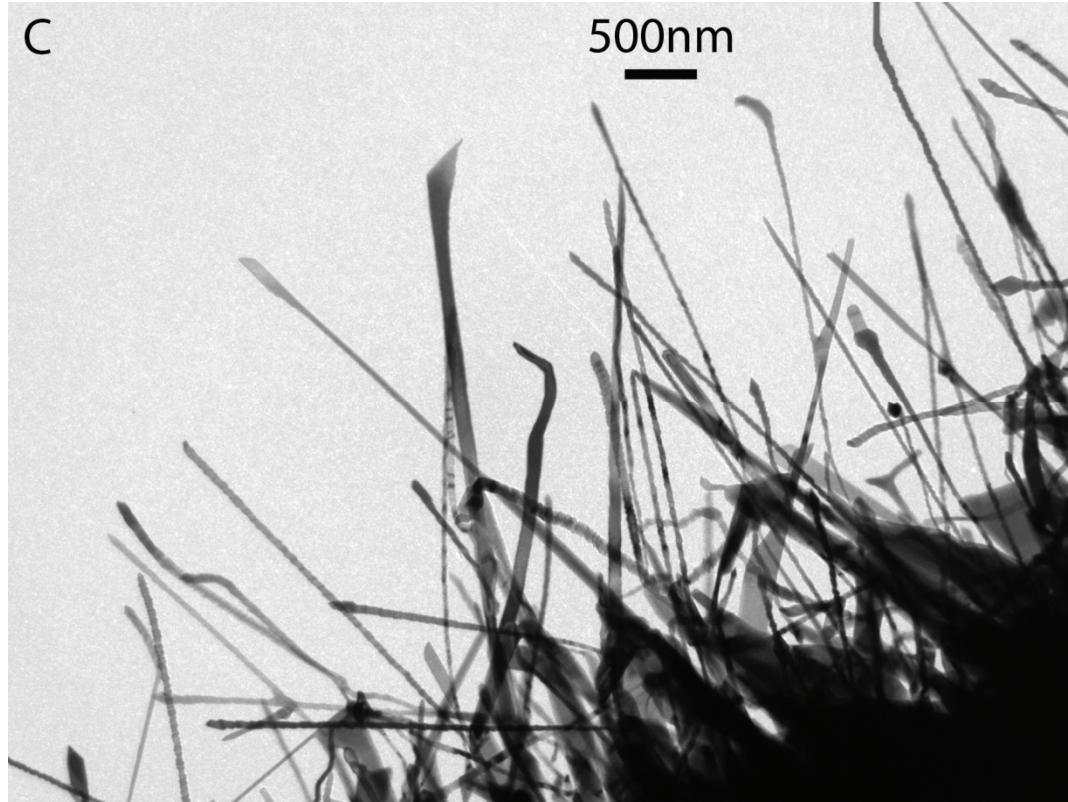
Figure 6.14: A and B are low magnification SEM images of Ti TEM grids oxidized while laying on a polished alumina substrate at 700°C for 4hours at a flow rate of 500scm wet argon. Insets in B show higher magnifications of the corresponding regions outlined with white boxes.



continued

Figure 6.15: SEM (A and B) and bright field (BF) TEM (C) micrographs of Ti TEM grids oxidized vertically at 700°C for 4 hours at a wet argon flow rate of 500scm.

Figure 6.15: Continued



6.6 Nanowire Structure and Morphology Characterization

Knowing the impact of various processing parameters is the first step in understanding the formation of nanostructures by oxidation in wet argon. However, to be a useful technique one must also know what material is being formed. It has been documented in the literature that oxidation in an oxygen rich environment, such as water vapor, forms titanium oxide. Daothong *et. al.* reported the formation TiO_2 nanowires by oxidation in the presence of ethanol vapor. Through analysis via Raman Spectroscopy both the anatase and rutile polymorphs of TiO_2 were observed. Likewise, Peng *et. al.* produced TiO_2 nanostructures by oxidizing Ti sample in a variety of atmospheres including

HCOOH, CH₃CH₂OH, CH₃CHO and CH₃COCH₃. XRD analysis showed only the rutile phase of TiO₂ present for all oxygen environments. It was prudent to investigate the titanium oxide phase(s) present in the nanostructures grown by oxidation of CPTi in wet argon. **Figure 6.16** presents XRD data acquired from CPTi foils oxidized in a humid environment. Samples oxidized at 600°C show a mixture of rutile TiO₂, TiO, and α titanium. Oxidation temperatures of both 700°C and 800°C produced only rutile TiO₂. An increase in the relative peak intensities was observed for samples oxidized at 800°C compared to the 700°C samples.

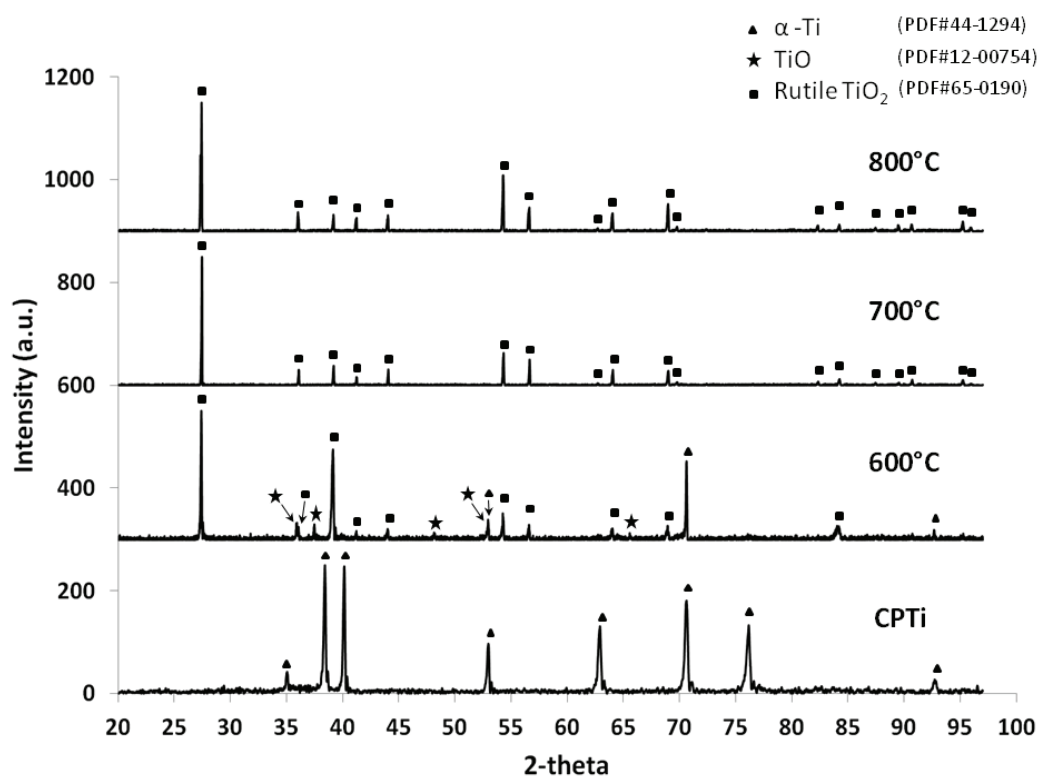


Figure 6.16: XRD spectra of commercially pure titanium samples oxidized at 600°C, 700°C, and 800°C for 6 hours at a wet argon flow rate of 500 sccm.

The XRD analysis showed the oxide film formed by oxidation of commercially pure titanium in wet argon to be the rutile phase of TiO_2 . However, this is a bulk analysis technique which collects data from the entire surface of the sample that is exposed to the x-rays. One cannot say determinately from the XRD data alone that the resulting nanostructures are rutile TiO_2 . Structural characterization specific to the NWs must be performed to confirm their crystal structure. An ideal analysis technique for this investigation is electron diffraction in the TEM. The following section discusses the analysis of two of the nanostructures produced by the oxidation of CPTi in a humid environment by TEM; ribbon and stacked NWs.

6.6.1 TEM investigation of Ribbon and Stacked Nanowires

With the successful growth of NWs on the CPTi TEM grids direct analysis via TEM was possible. When oxidized in wet argon Ti TEM grids produce two main morphologies of nanostructures, nanoribbons and stacked NWs. Both structures, when grown on Ti TEM grids, were found to be only 10 – 100s of nanometers thick and thus electron transparent making them suitable for TEM characterization without further processing. **Figure 6.17 A** shows a relatively low magnification view of this mixed nanostructured growth. Several of the ribbon type morphologies are noted with arrows and the ribbon identified with the number 1 is highlighted in **Figure 6.17 B** and is the focus of the following discussion.

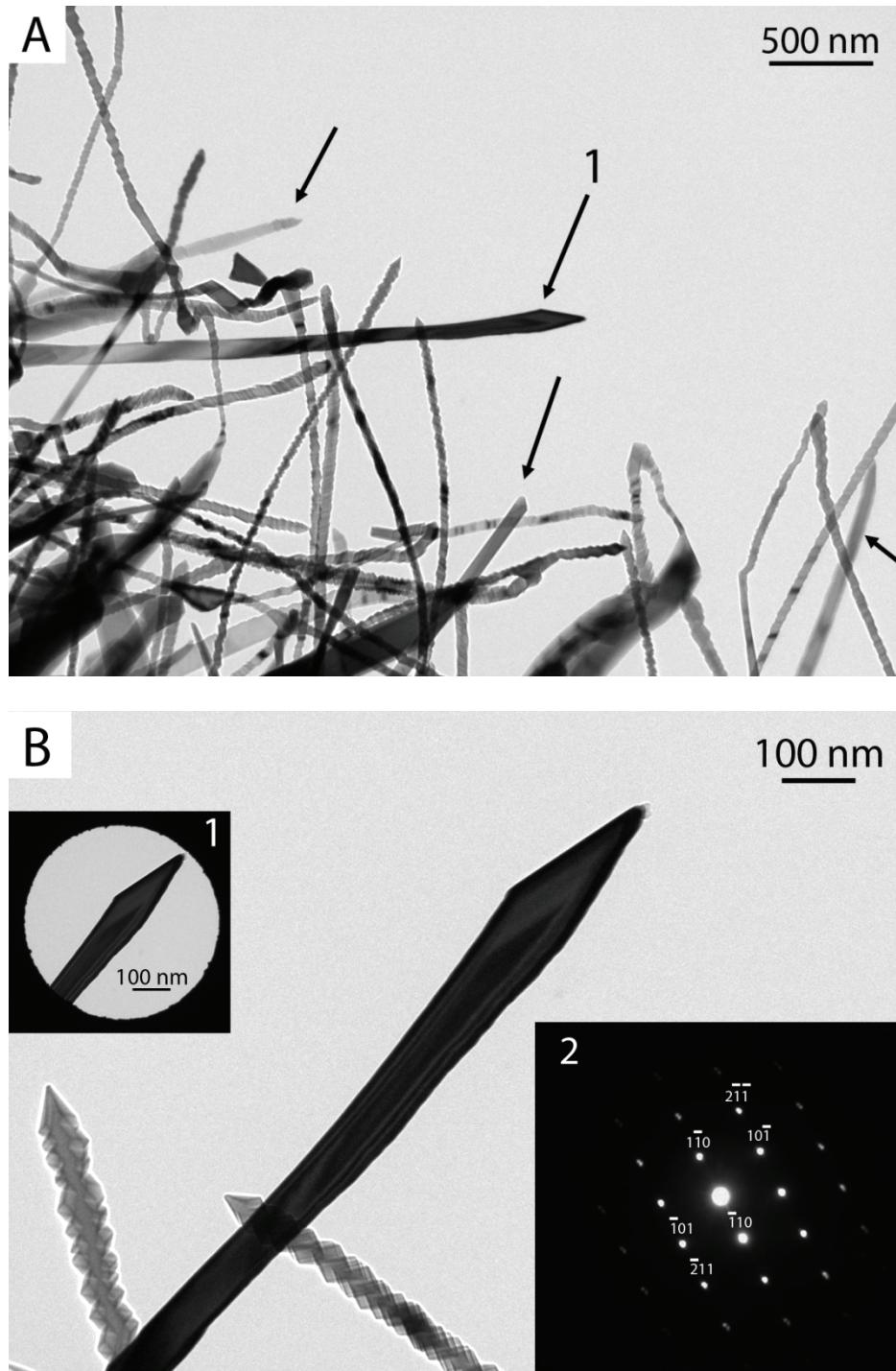


Figure 6.17: Bright field TEM images of a ribbon structure grown on a Ti TEM grid A) surrounded by other nanostructures and B) higher magnification of the nanoribbon with inset showing the SA aperture only on the ribbon and inset 2 the corresponding SAD pattern indexed to be rutile TiO_2 with a zone axis parallel to $[111]$.

6.6.2 Nanoribbons

To obtain strong diffracting conditions for the nanoribbon of interest, the sample was tilted in BF TEM mode with the objective aperture (OA) inserted and centered until the nanoribbon of interest appeared dark indicating strong diffraction was occurring. At this point the nanostructure was thought to be relatively near a zone axis. The standard method for locating zone axis through the use of Kikuchi lines was not applicable in these samples due to the ultra thin nature of the structures. Once the ribbon was thought to be on or near a zone axis the selected area aperture (SA) was inserted and centered on the nanoribbon (**Fig. 6.17 B inset 1**) such that a selected area diffraction (SAD) pattern could be obtained from the ribbon (**Fig. 6.17 B inset 2**). The SAD pattern showed the nanoribbon to be rutile TiO₂ with a [111] type zone axis. A sequence of low index **g**-vectors was used for dark field (DF) imaging of the nanoribbon. The results are presented in **Figure 6.18** where the circled diffraction spots correspond to the actual spot which was moved into the OA through diffraction shift. In a DF image, the features which show bright against a dark background are contributing to the diffraction spot selected. Since all of the diffraction spots selected for DF imaging came only from areas of the selected ribbon it can be concluded that these spots are all from this nanostructure. That is, the ribbon is a single crystal. This information gives confidence that the ribbons structure is indeed rutile TiO₂. The bright bands seen in the DF images of **Figure 6.18** are indicative of thickness fringes. The ribbons thickness is not uniform along its width but rather is wedge shaped or tapered at its edges.

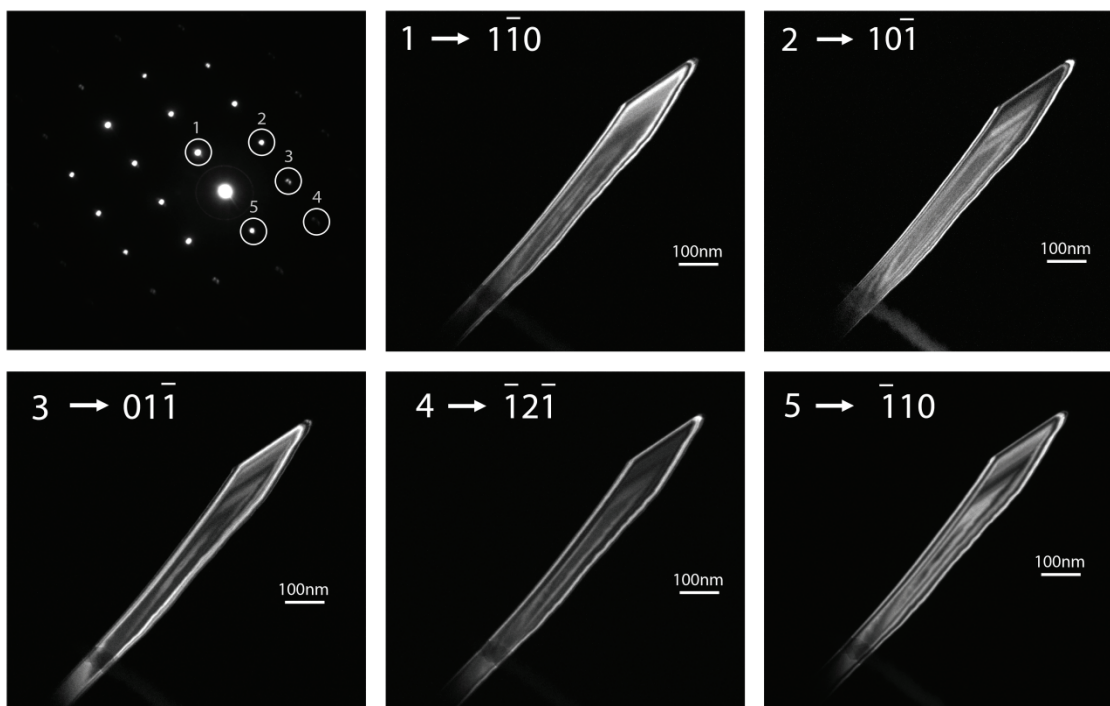


Figure 6.18: DF TEM images of TiO₂ nanoribbon obtained by selecting a sequence of low index **g**-vectors.

Growth direction information for a NW can be obtained from a TEM image and SAD pattern pair if the NW is orthogonal to the electron beam. If the NW is orthogonal to the beam and appropriate instrument calibration is taken into account, specifically the change in image orientation with change in magnification, the growth direction can be determined by finding a row of diffraction spots which are parallel to the NW axis.

Figure 6.19 demonstrates this by superimposing the nanoribbon observed in **Figure 6.17** with its corresponding diffraction pattern. The superimposed image was made in post processing by reducing the transparency of the ribbon image by 50% thus allowing the SAD underneath to be seen. The ribbon's axis is observed to be parallel to the $\langle 101 \rangle$

family of diffraction spots thus, this appears to be its growth direction. However, one can only be confident in this analysis if the ribbon is truly orthogonal to the electron beam. This ribbon grew out radially from a 300 μm thick TEM grid. It is unlikely that it grew perfectly perpendicular to the grid, which is orthogonal to the electron beam. For this reason, this one set of image and SAD pattern cannot be used conclusively to determine growth direction. To complete this analysis, an additional SAD pattern from the same wire tilted such that a different zone is being diffracted is necessary. Once a second row of parallel diffraction spots has been obtained from a different zone axis, the cross product of the Miller indices of these two planes will be the true growth direction. Due to time constraints, this analysis has not yet been completed.

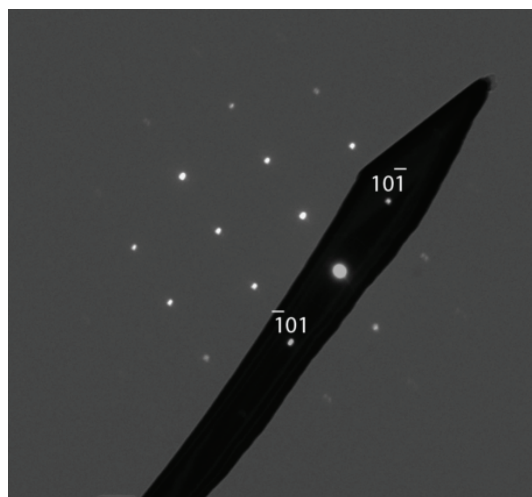
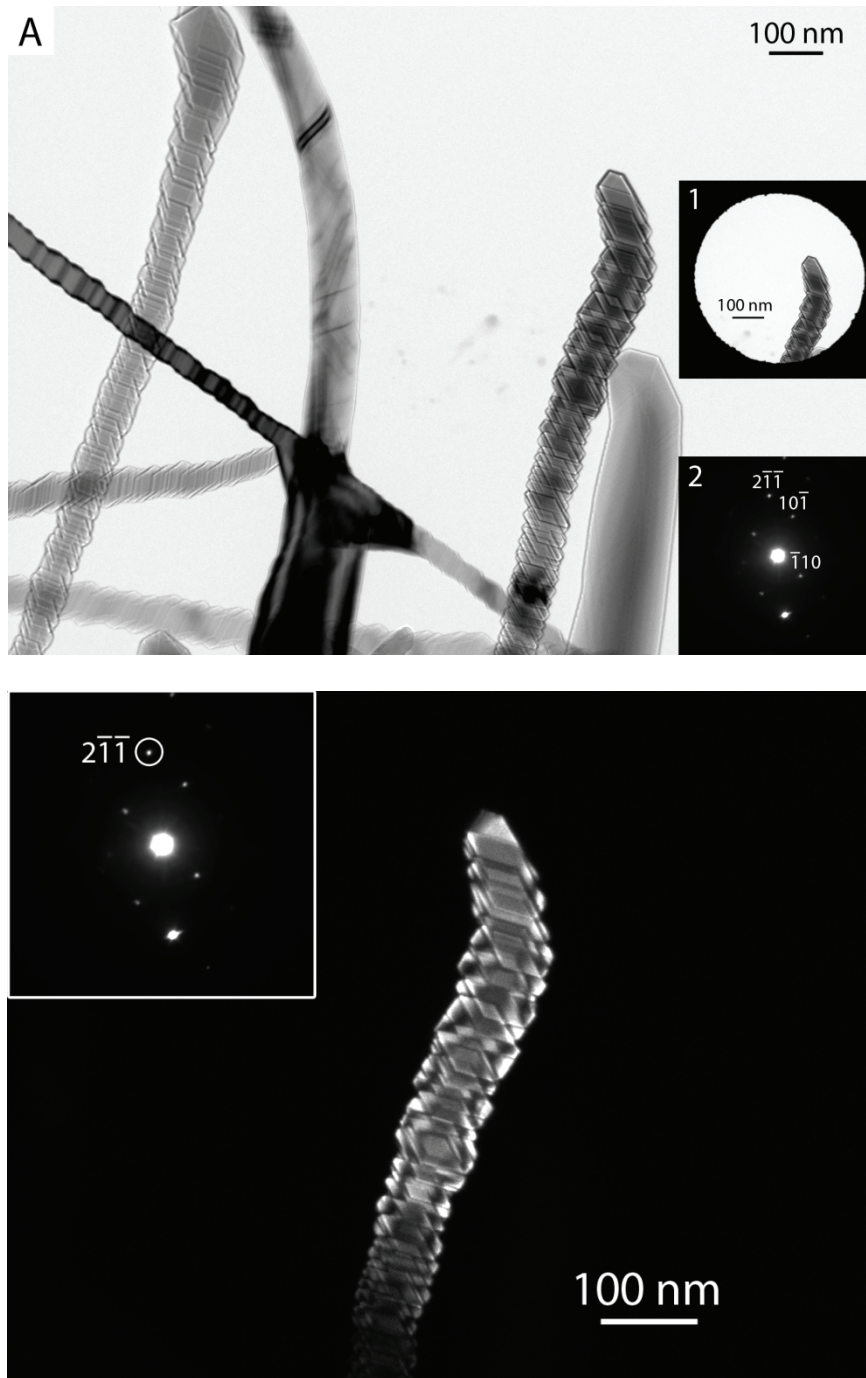


Figure 6.19: BF TEM image of nanoribbon superimposed onto the corresponding diffraction pattern to determine a growth direction of $\langle 101 \rangle$ of rutile TiO_2 . The ribbon image has been set to 50% transparency in post processing to form this image.

6.6.3 Stacked Nanowires

Stacked NWs were also observed as a result of the oxidation of CPTi TEM grids in the wet argon as can be seen in **Figure 6.17**. These were also excellent candidates for analysis via TEM. A BF TEM image of a stacked NW is shown in **Figure 6.20 A** with its corresponding diffraction pattern (**inset 2**). Inset 1 of this image shows that only the stacked NW was selected to obtain the diffraction pattern presented in inset 2. The sample was tilted such that strong diffraction was occurring however; the pattern was not exactly on zone. It was still possible to index the pattern to a [111] type zone axis of rutile TiO₂. This is the same crystal structure and orientation observed for the nanoribbon in **Figure 6.17**. A DF image of the stacked NW obtained using the 2-1-1 **g** vector indicates the NW is a single crystal of TiO₂ (**Fig. 6.20 B**). By superimposing the BF NW image onto the SAD pattern a first approximation of the NW growth direction was obtained (**Fig. 6.20 C**). It was again the <101> type direction as was identified for the nanoribbon in **Figure 6.19**.



continued

Figure 6.20: A) BF TEM image of stacked NW structure grown on CPTi TEM grid by humid oxidation. Inset 2 in A) shows $[111]$ rutile SAD pattern obtained from region in inset 1. B) DF image of the stacked NW obtained from the $2-1-1$ g indicating the NW is single crystal. C) BF image overlaid on SAD to identify NW growth direction.

Figure 6.20: Continued

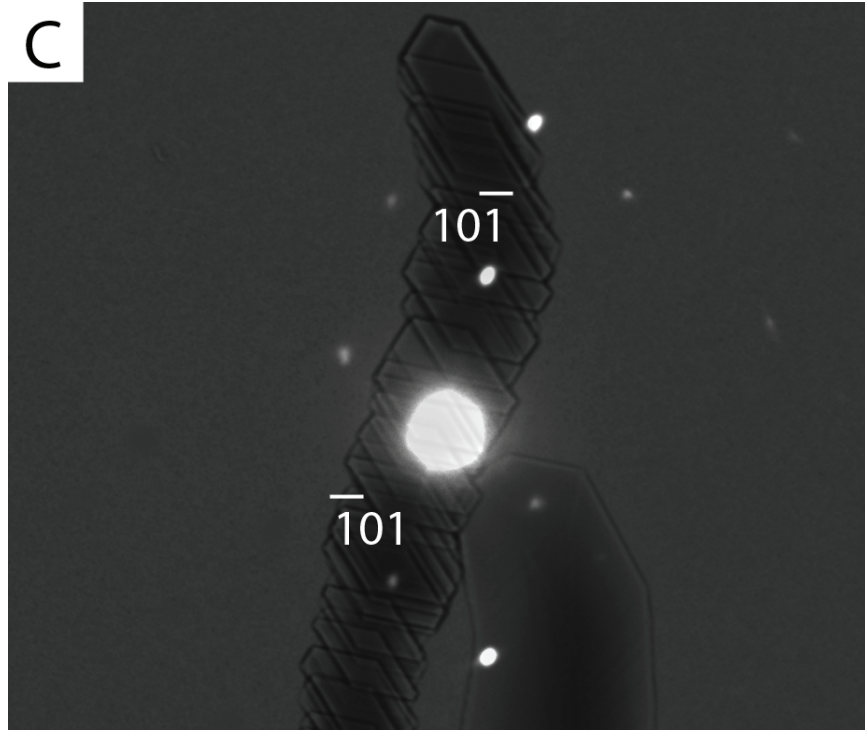
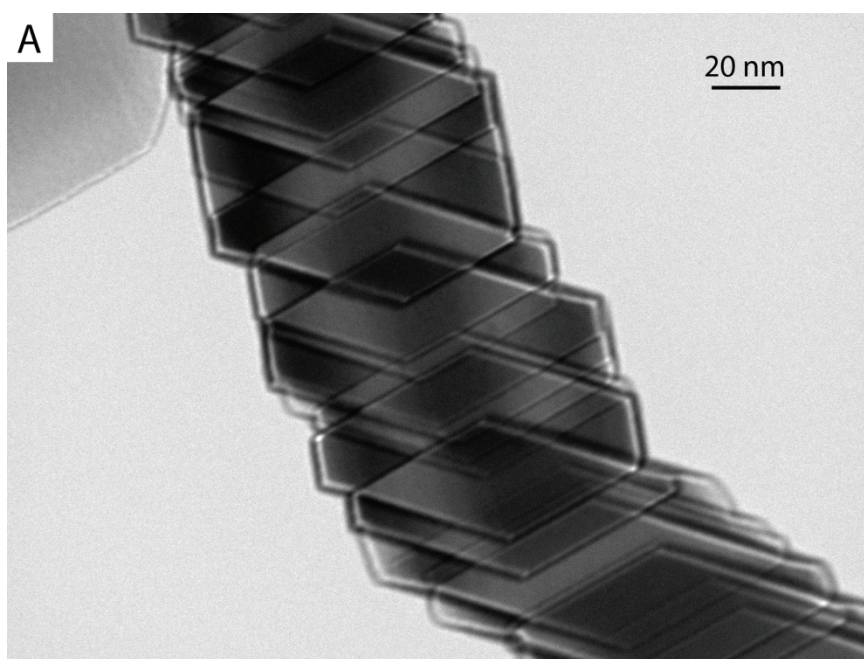


Figure 6.21 shows high magnification images of a small portion of this wire. Features that look like individual crystal platelets can be observed along the length of the NW. The corresponding DF image observed in **Figure 6.21 B** confirms the single crystal nature of the NW. The contrast observed is most likely due to thickness variations between alternating layers. The morphology seen in the TEM is consistent with the results obtained by SEM analysis in **Figure 6.10**.

The stacked NW featured in **Figure 6.20** has a bend near its tip where the wire axis appears to change. A high magnification BF TEM image of this bend shows that a change in the NW morphology or structure is not the cause for the change in direction (**Fig. 21 C**). Instead, a slight elongation (~ 10 nm) of a few stacked platelets at the start of the bend

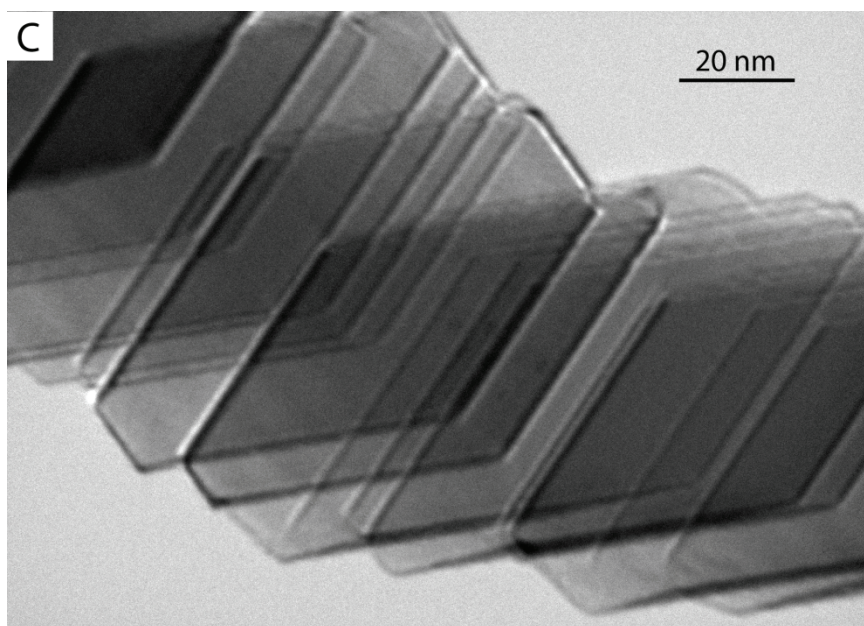
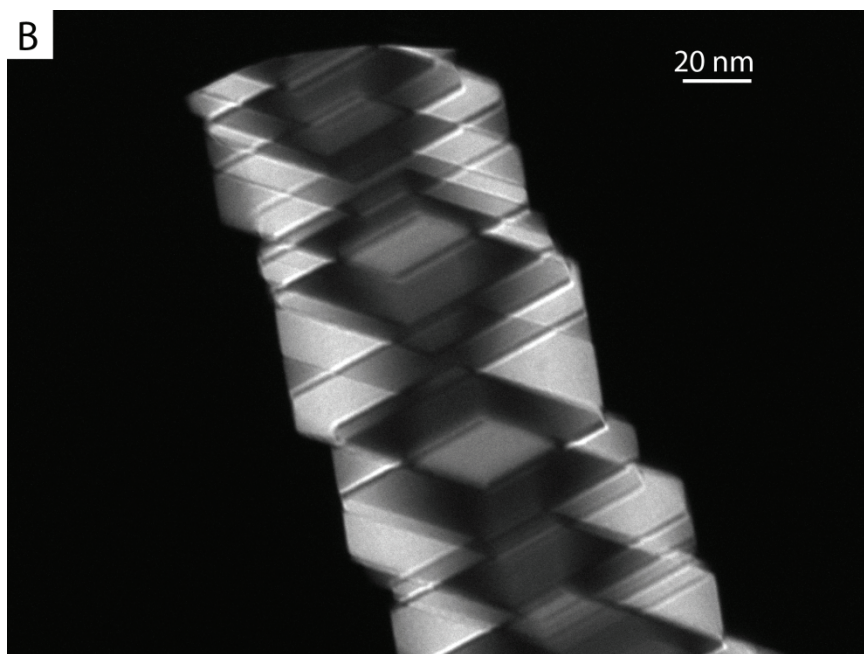
is observed. This elongation appears to only occur for a very small number of platelets however, subsequent platelets continue to grow at the new angle. To visualize what is happening one can imagine a deck of playing cards, where one card is being stacked one on top of another. If a card with a slightly increased length is placed on top of the deck one or both of its ends would over hang the cards below it. If the next card was placed on top such that it was lined up with one of the overhanging sides a slight shift would be observed. If this happened over several cards a bend in the stack of the cards would be seen. This is what appears to be happening in the bend of the stacked type NW.



continued

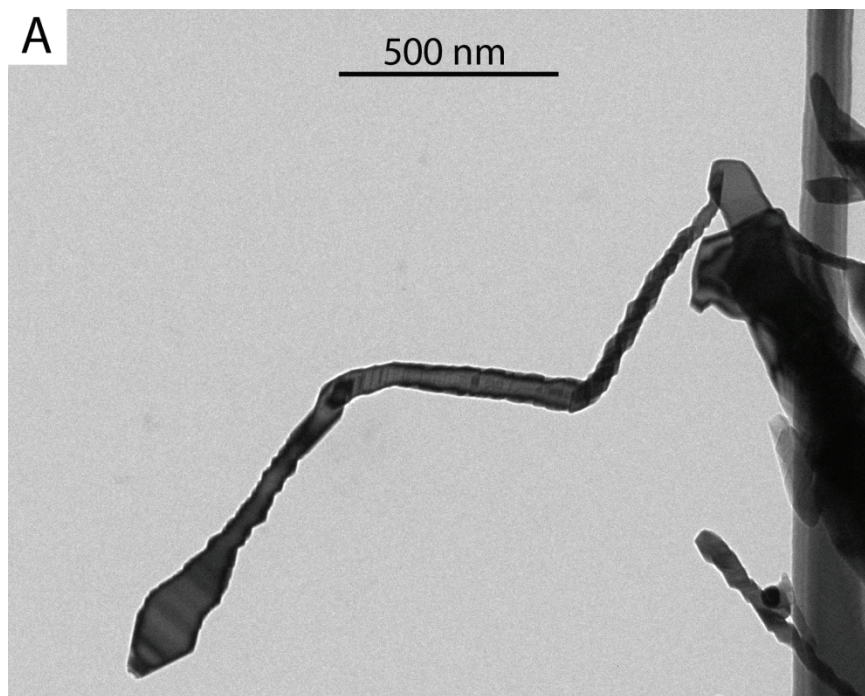
Figure 6.21: High magnification TEM images of stacked NW structure highlighting the stacked morphology both in (A & C) BF and B) DF imaging modes. The same 2-1-1 g was used for the DF image in B

Figure 6.21: Continued



Another stacked NW has been imaged using a TEM in **Figure 22**. Again, sharp turns can be observed along the length of the wire. When magnified, the stacked structure

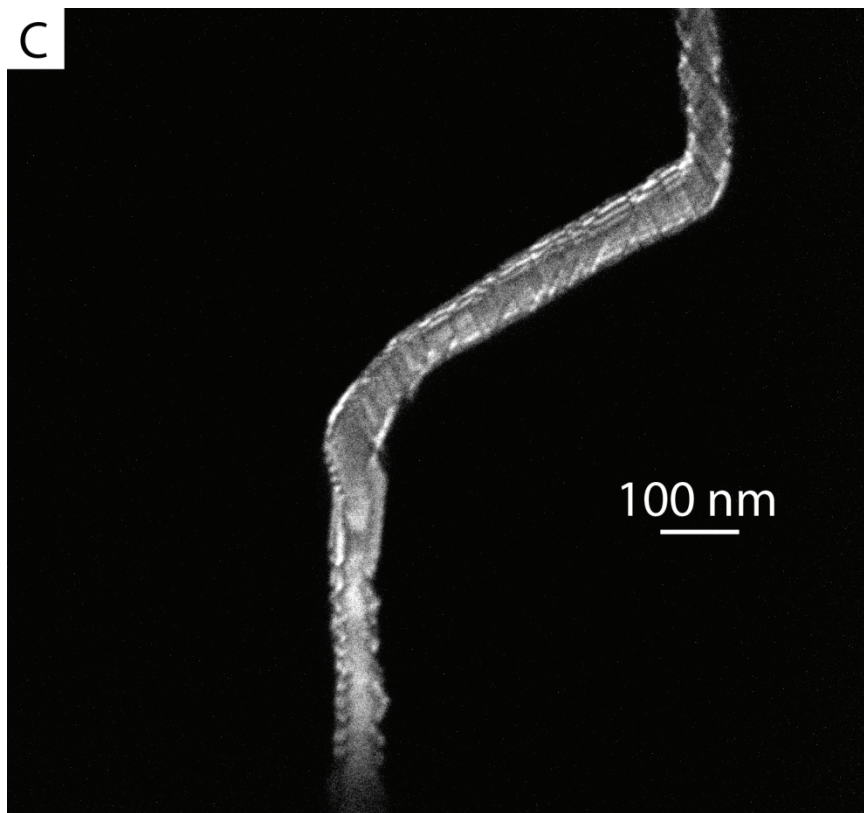
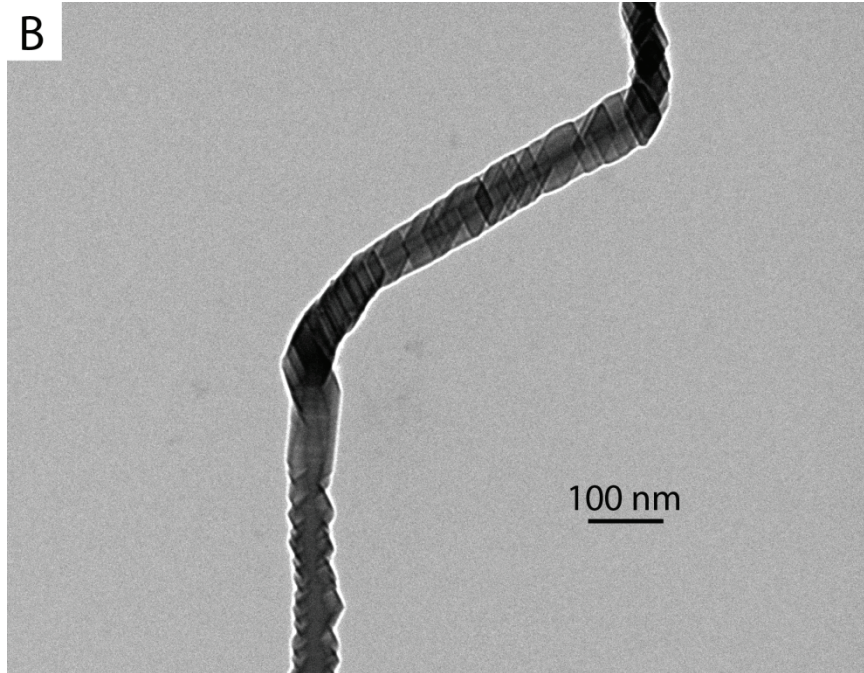
previously observed becomes apparent and continuous leading up to the second bend (Fig. 22 B). Imaging in DF mode shows the entire length of the NW, through both turns, to be single crystal. This has been observed time and again in these structures. Though the morphology of the wires and the severity of the turns they make vary from sample to sample they always appear to be single crystal structures. What exactly the cause of this change in growth direction is unknown, but is worthy of further investigation.



continued

Figure 6.22: A) Low magnification and (B & C) higher magnification TEM images of a stacked type NW having multiple bends. The DF image in C shows the entire length of the NW through both bends is single crystal.

Figure 6.22: Continued



6.7 Conclusions

The oxidation of CPTi substrates in wet argon has been shown to drastically increase the growth rate of oxide nanostructures compared to oxidation in a low oxygen environment. Various oxidation parameters were investigated including the oxidation temperature, duration, and gas flow rate. Nanostructured oxides were observed resulting from a wide combination of growth parameters however some trends were identified. As the oxidation temperature increased, the average size of the oxide structures increased. Also, as the flow rate of the gas bubbled through DI water increased, an increase in the density of the resulting structures was observed. At long oxidation times 3-D networks of nanostructures were observed. A more detailed study on the formation of the 3-D networks is warranted as this could be a useful morphology for certain applications. A wide variety of structures were observed after the oxidation of Ti samples. These include micron sized rods and plateau type structures such as ribbons, where two dimensions were micron in scale while the third was in the nanometer regime, as well as stacked and zigzag type NWs. Additionally, structures were observed where the growth direction had changed drastically during oxidation even to the point where a loop of a single NW was formed. Nodes were observed where two or more nanostructures came together and/or grew apart. Further analysis is necessary to determine what conditions favor the growth of one morphology over another. It is also unclear what would cause a NW to make a +90° turn during oxidation. An understanding of how and why nodes form would also be desirable. They have been observed forming from a single NW out of which several new wires form.

It has been demonstrated that nanostructures grown on CPTi TEM grids by oxidation in wet argon can be characterized directly in the TEM. Nanoribbons were shown to be single crystal rutile TiO_2 through a combination of SAD and DF imaging techniques. A possible growth direction for the nanoribbons has been identified as $\langle 101 \rangle$ by superimposing a BF TEM image of a nanoribbon onto its SAD pattern and locating a row of diffraction spots parallel to the axis of the nanoribbon. This is not sufficient information to completely identify the growth direction of the nanoribbon. For this one BF image/SAD pattern pair to be conclusive for growth direction investigation, the nanoribbon is required to be completely orthogonal to the electron beam. For nanostructures grown by this process on TEM grids it is highly unlikely that they are orthogonal to the electron beam. They are growing outward from a curved surface and have been observed making several bends and turns throughout their growth process. Thus, they are most likely inclined or declined at some angle to the electron beam. To concisely identify the growth direction and additional SAD pattern from a different zone should be obtained by tilting the specimen. Once a growth direction is obtained from the second SAD pattern, the cross-product of the two growth directions should be taken. The resulting vector would conclusively be the growth direction for the nanostructure.

TEM analysis of stacked NWs grown on the CPTi TEM grids identified the NWs to also be single crystal rutile TiO_2 . Using similar analyses the growth direction, to a first approximation, was also identified to be $\langle 101 \rangle$. Additionally, high magnification of a bend in the NW showed it to consist of alternating platelets with a slight shift from one

layer to the next. By continuing this shift over several platelets a curved feature was formed.

This growth process is ripe for future studies. Little is known about the mechanisms governing the production of the observed structures. While several different oxide morphologies have been produced by this process the conditions which promote the formation of one morphology over another are not understood. Many of the morphologies are electron transparent as-grown and are therefore excellent candidates for characterization via TEM. Preliminary TEM analysis has been performed but additional studies are required to fully characterize the nanostructures. One example of this is the need to complete the characterization of NW growth direction. Although the structures described in this chapter have not yet been completely explored and understood, they are useful platforms for further investigation and applications. The following chapter discusses some of the applications being pursued for both the nanostructures produced on CPTi by oxidation in wet argon and those produced on Ti alloys by oxidation in a low oxygen environment.

Chapter 7: Applications and Extensions

7.1 Introduction

It has been demonstrated that nanostructures can be grown on Ti and Ti alloys by oxidation. For growth on Ti alloys, a low oxygen environment produces a high density of nanowires (NWs) covering the surface of the metal. Commercially pure Ti (CPTi) produces only very small NWs in the low oxygen oxidation process however it has been demonstrated that by introducing water vapor into the reaction chamber during oxidation well defined nanostructures form. While each of these processes and their resulting nanostructures are scientifically interesting and merit in-depth studies and evaluation, they are only truly useful if they can be employed to improve an existing device or solve a problem. To this end several applications for the oxide nanostructures are currently being investigated including platforms for chemical sensing, coatings to increase cell adhesion and proliferation, sources for improved x-ray emissions, and as platforms for further functionalization into ferroelectric materials. Each of the following sections is devoted to the discussion of ongoing application investigations for the nanostructures discussed in Chapters 4 and 6 of this manuscript. Current results and future directions are discussed and specific challenges are highlighted.

7.2 Experimental

Metallic samples and sample preparation techniques used for the Ti alloys and CPTi samples are the same as those reported in the previous chapters (Ti alloys - Chapter 4 and CPTi - Chapter 6). Processes used to produce TiO₂ nanostructures also follow the steps outlined in the respective chapters for each material. If significant alterations to these processes occurred, they are mentioned in the appropriate application sections.

Surface morphology was characterized in a high resolution FEG-SEM (Model Sirion, FEI, Oregon). Prior to SEM characterization, most samples were coated in a thin layer of Au using a sputter coater (Model 3 Sputter Coater 91000, PELCO) at a plasma current of ~15 mA for 40 seconds. Those samples not coated were placed in a clip style mount for imaging via SEM. The clip mount was used when further processing of the sample after SEM analysis was necessary. Crystal structure verification was performed using XRD analysis (Scintag PAD-V and Bruker XD). Additional characterization and experimental techniques for a given application are discussed in the respective section.

7.3 Results and Discussion

The following sections outline the specific applications investigated for the TiO₂ nanostructures produced by the oxidation of Ti and Ti alloys. While this is not an exhaustive list of the potential applications for these structures it does highlight some of the applications currently under investigation by our research group and collaborators.

7.3.1 Sensor Fabrication – Alloy Particles & Thin Films

Improvement to chemical sensing technologies is of high importance due to the wide range of industries and applications which rely on this technology to optimize process

control, improve efficiency, and maintain a safe environment. Due to the increased surface area provided by the oxide nanostructures and the semiconductor properties of TiO₂, the low-cost simple growth processes used to produce these nanostructures are particularly suited for their use in chemical sensing.

7.3.1.1 Background

Metal-oxides, such as TiO₂, have been widely explored for chemical sensing of reducing gases such as H₂, H₂S, HCHO, CO and ethanol. This is due to the change in resistance that can occur because of surface interaction between adsorbed oxygen and these gases. A metal oxide will have some amount of adsorbed oxygen on its surface as oxygen ions O₂⁻, O⁻ or O²⁻, which extract electrons from the oxide producing an electron depletion layer at the surface of the oxide.[187] When a reducing gas such as CO is introduced a reaction between the CO and the O ions adsorbed on the oxide surface occurs. The oxygen ion bonds with the reducing gas releasing an electron back into the oxide reducing the size of the electron depletion layer. This results in a change in the resistance of the material. By measuring this change in resistance, one can determine the concentration of the reducing gas.[188] The depletion layer thickness is a function of both the specific metal oxide and the amount of adsorbed oxygen ions on the surface. However, if one can obtain a metal oxide morphology whose size is on the order of the depletion layer a small change in the layer due to the introduction of a low concentration of reducing gas would create a relatively large change in resistance for the material. Thus nanostructures have been gaining traction as platforms for chemical sensors.[189] TiO₂ has been of particular interest due to its chemical and structural stability at high

temperatures.[190] Nanostructured TiO₂ sensor platforms have been fabricated using a variety of methods including electrospinning, anodization, and nanocarving.[12, 143, 191] Additionally, our research group has extensive experience with the fabrication and testing of chemical sensors. As such, chemical sensing was a logical choice as a first approach to demonstrating a useful application for the NWs grown by oxidation of TI alloys.

7.3.1.2 *Results*

Initially, nanostructured reducing gas sensors were fabricated by depositing Ti555 powder onto an alumina substrates pre-patterned with Au interdigitated electrodes. The samples were then placed in a reaction chamber and oxidized to produce nanostructured samples. Characterization via SEM was then performed to ensure nanostructured growth occurred. Initial results were promising for these sensors as NWs were easily observed coating the surface of the Ti555 particles. However, particle adhesion to the alumina substrate was poor causing the oxidized particles to fall off before any sensing measurements could be performed.

To improve particle adhesion a paste was made using the following ingredients: Heraeus V-801 glue, Heraeus RV-507 solvent, ethanol and Ti555 particles. This paste was mixed and painted onto the interdigitated electrodes. The painted samples where then dried in a vacuum oven for two hours before being annealed in air at 400°C for 4 hours at a ramp rate of 2°C/min to burn off the organic binders used in the paste formation. This burnout process also increased adhesion of the particles to the interdigitated alumina substrate. Once the burnout process was complete the samples were oxidized to promote NW

growth using the standard Ti alloy oxidation procedure previously outlined in Chapter 4. The only modification made to the oxidation procedure was a significantly slower temperature ramp from 23°C/min in the bulk alloy work down to 8°C/min for the sensors to reduce thermal stresses during ramping with the goal of maintaining a strong adhesion between the particle film and the substrate. **Figure 7.1** shows a schematic of the sensor fabrication process.

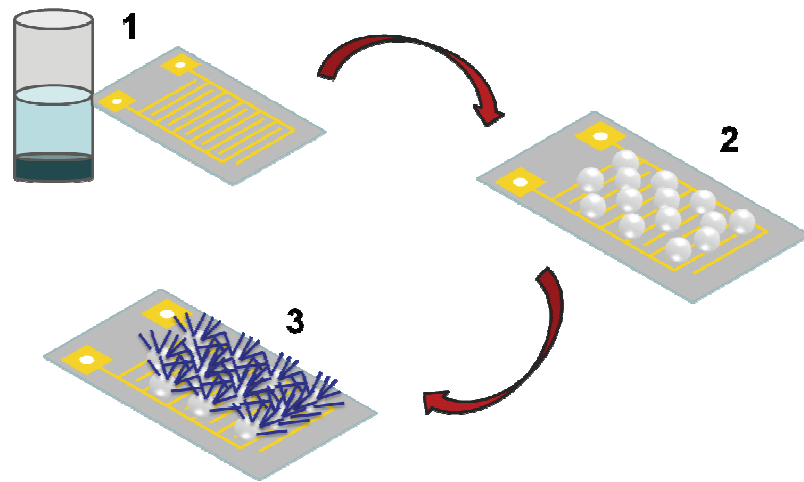


Figure 7.1: Schematic showing the steps for fabricating the nanostructured TiO₂ sensor using Ti555 particles. 1) Preparation of paste containing Ti5-5-5 particles and bonding agents. 2) Application of the paste to a substrate containing interdigitated electrodes. 3) Oxidizing of the as-deposited particles to produce interconnecting NWs.

An SEM image of the as painted particle film on the Au interdigitated electrodes can be observed in **Figure 7.2**. The average particle size is approximately 100 μm while the gaps between adjacent electrode fingers are 275 μm. This requires several particles to be in contact with one another for an electrical connection to be made. **Figure 7.3** clearly shows multiple particles in contact with one another bridging the electrode gap post

oxidation. This image (**Fig. 6.3**) was taken near the edge of the sensor where the particle load was relatively low. The coverage of Ti5-5-5 particles is much improved near the center of the sensor as shown in **Figure 7.5**.

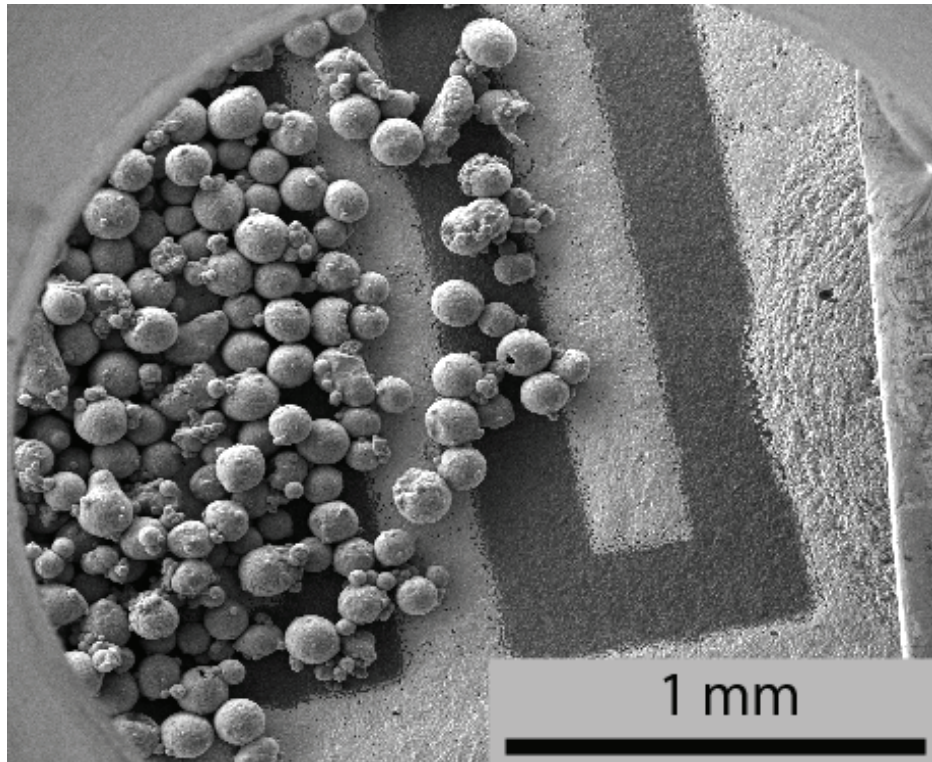


Figure 7.2: SEM image of the as-deposited particle paste after organic binder burnout on an Au interdigitated electrodes substrate. The white lines are the Au electrodes.

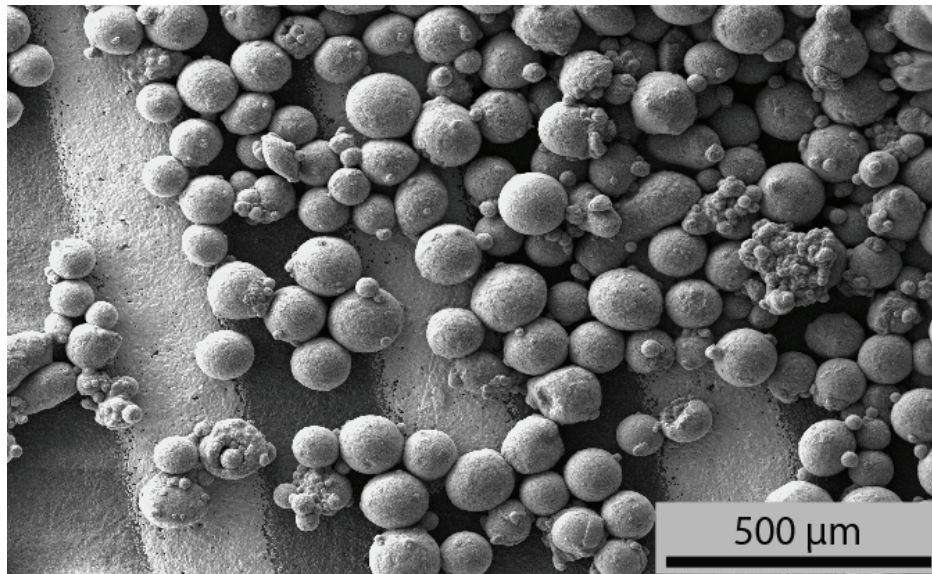


Figure 7.3: SEM micrograph taken at the edge of the sensor showing particle bridging of interdigitated electrodes.

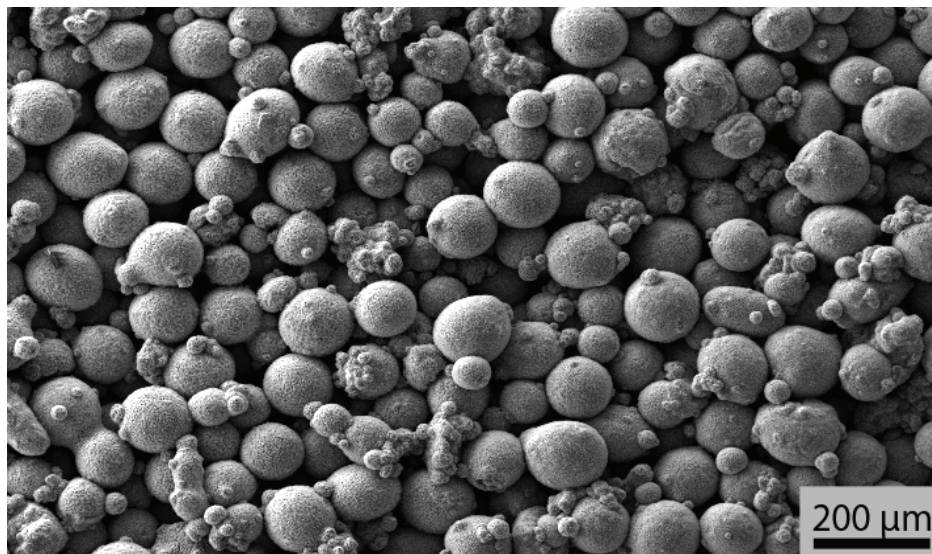


Figure 7.4: SEM image taken near the center of the sensor post oxidation anneal showing wall to wall coverage of the oxidized Ti555 particles.

The as-deposited particle film was oxidized for 16 hours at 700°C in 500 sccm of flowing Ar to produce TiO₂ NWs. These processing parameters yielded complete NW coverage of the sample. **Figure 7.5 A** shows a representative low magnification image of the nanostructured growth resulting from this process. To maximize the benefit of metal-oxide nanostructures for chemical sensing (i.e. taking advantage of the large depletion layer) the particle-to-particle electrical connection should be from NW to NW. To best achieve this, the particles should be even spaced sufficiently apart such that the as-grown NWs bridge the gap and grow into one another. However, using the thick film method for sensor fabrication does not allow for this level of precise particle placement during sensor construction. The next best form of electrical contact would be to have the nanostructures growing outward from the particles grow into an adjacent particle as shown in **Figure 7.5 B**. Here multiple particles can be observed with interpenetrating NW growth. It may be possible to further enhance this interpenetrating growth by increasing the oxidation duration.

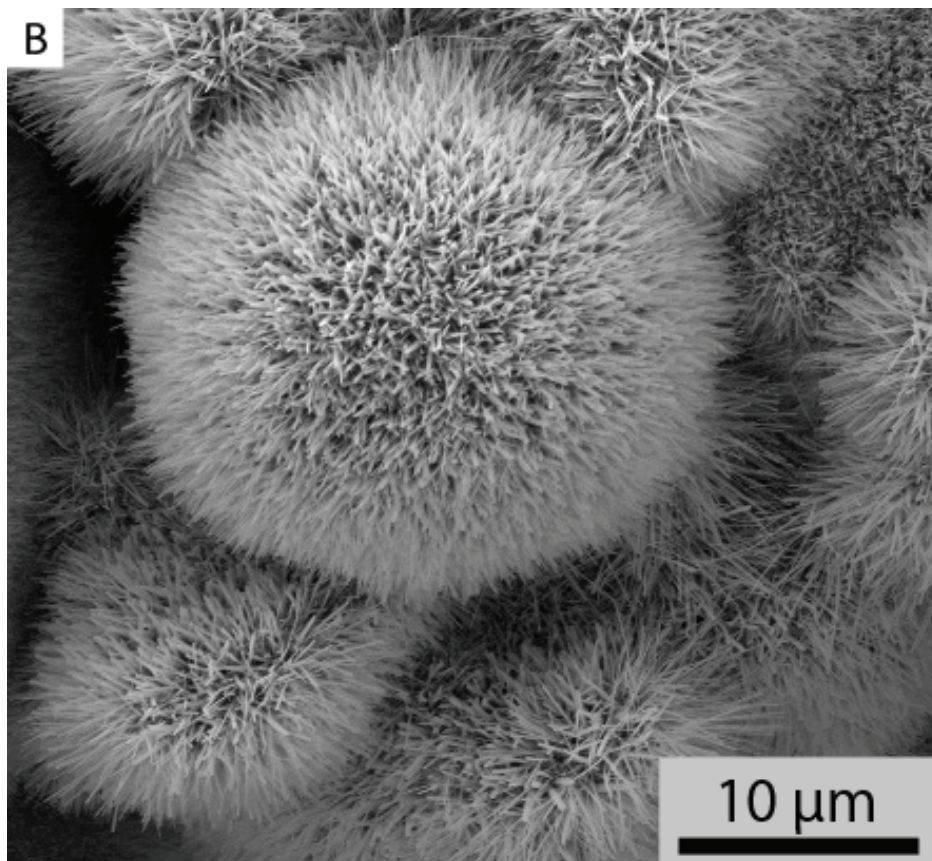
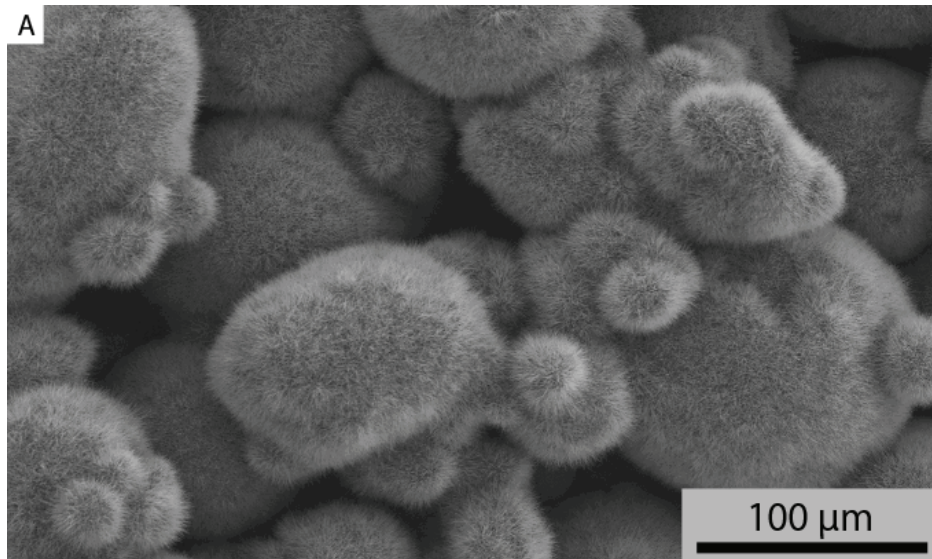
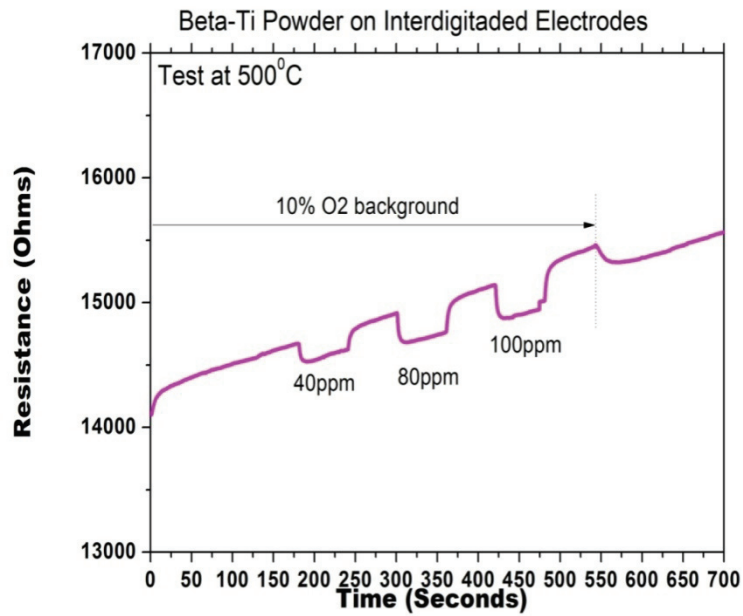
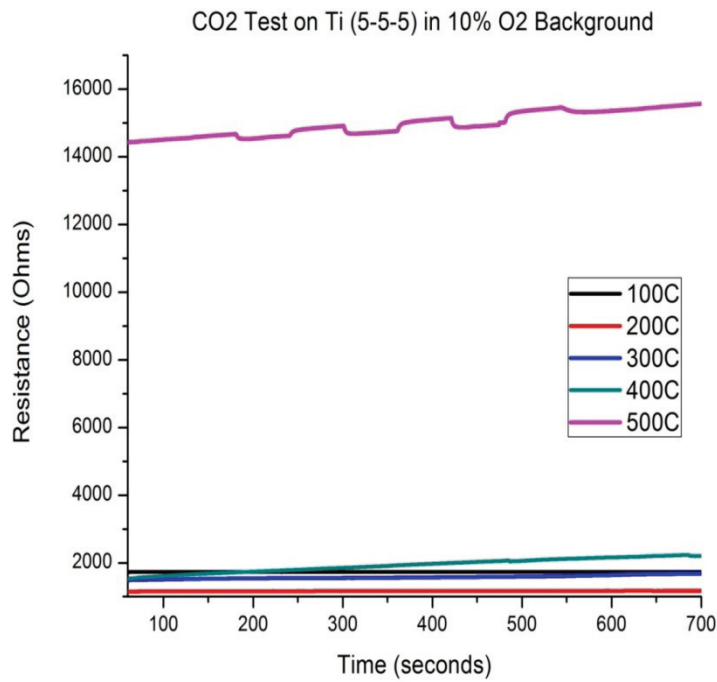


Figure 7.5: SEM images A) showing complete NW coverage and B) NW inter particle connections on Ti5-5-5 particle film resulting from oxidation at 700°C for 16 hours in 500 sccm of flowing Ar.

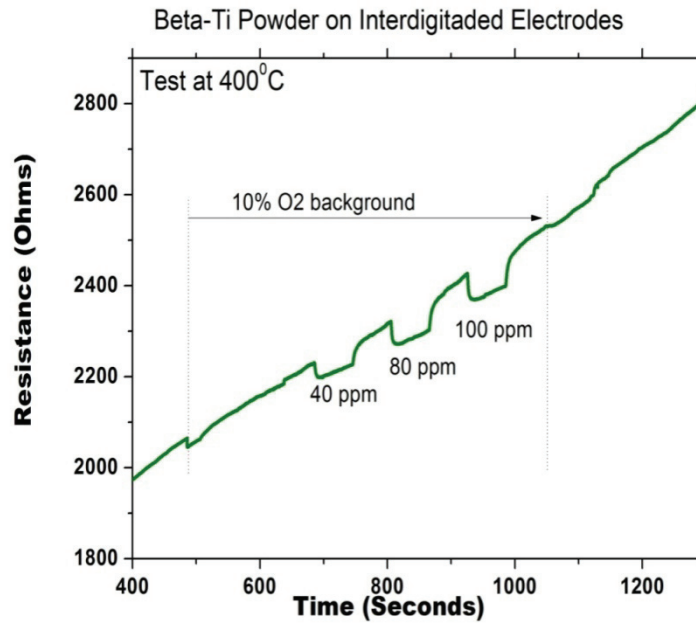
The actual testing of the thick film Ti5-5-5 particle based sensors was performed in a horizontal tube furnace to allow for both atmospheric and temperature control. Various concentrations of carbon monoxide (CO) gas were introduced into the reaction chamber while the resistance of the sensor was monitored. The CO atmosphere was controlled by balancing a standard concentration of CO with nitrogen while maintain a 250 sccm overall flow rate. A background of 10% oxygen was maintained throughout sensor testing. The sensor response to 40 ppm, 80 ppm, and 100 ppm CO was tested over a range of temperatures (100 – 500°C). The testing temperature was held for 3 hours prior to introduction of the background gas to minimize the effects of changing temperatures. **Figure 7.6 A** is a plot of the changes in resistance of the Ti5-5-5 particle based sensor with change in CO concentration. Multiple sensor test temperatures are plotted on the same graph. There are multiple pieces of data in this plot worth noting. First, little to no change in resistance was observed in the low temperature tests (100-300°C). Second, a change in resistance with a change in CO concentration is only apparent for the 500°C test. However, a significant drift in the baseline resistance of the sample in both the 400°C and 500°C test is observed. Additionally, a significant change in baseline resistance was observed when the testing temperature was increased to 500°C. **Figure 7.6 B** is an isolated view of the 500°C sensing results including the CO concentrations tested. A sharp and increasing change in sensor response is observed at each step of increased CO concentration. A similar plot for testing at 400°C can be observed in **Figure 7.6 C**. Again, a sharp change in resistance with the introduction of increasing amounts of CO was observed. No change in resistance was noted at temperatures below 400°C.



continued

Figure 7.6: A) Plot of Ti5-5-5 particle based sensor response change in CO concentration over a range of temperatures. B) Isolated sensor results for tests at 500°C and C) 400°C.

Figure 7.6: Continued



While both the 400°C and 500°C sensor tests showed a change in resistance with the introduction of CO both tests also had a significant increase in the baseline resistance throughout the testing cycle. In the 500°C test, the background is observed to drift by more than 1.5 kΩ throughout the test. This is most likely due to continued oxidation of the Ti5-5-5 particles. Prior to sensor testing they were oxidized in a low oxygen environment (sub 100 ppm O₂) for 16 hours at 700°C. It was believed that this would be sufficient to eliminate further oxidation at such low temperatures. What was not taken into account was the drastic increase in oxygen concentration used as the background for sensor testing. It was an increase from 100 ppm to 100,000 ppm. As discussed in previous chapters, the oxidation rate of titanium is a function of both the oxidation temperature and the oxygen environment. Additionally, in the study of the effects of

oxygen concentration in the oxidation of Ti alloys discussed in Chapter 4, an increase in the rate of oxygen consumption was first observed at 400°C. At lower temperatures oxygen was consumed at a very low rate. As the oxidation temperature was increased past 400°C a corresponding increase in the rate of oxygen consumption was observed. This is the behavior observed in both the 400°C and 500°C sensor tests. The rate of resistance increase in the 400°C tests was only ~40 Ω/min while the rate of increase in the 500°C test was nearly 125 Ω/min. This points to continued oxidation as the most likely reason for the drifting baseline resistance. To minimize this in future studies a two pronged approach should be used. First, a reduction in the particle size would reduce the overall amount of material available for oxidation. Second, an increase in the duration of the oxidation to produce NWs would both yield longer NWs and increase the oxide penetration into the particles. The end result from both of these approaches would be to limit the availability of un-oxidized metal for sensor testing.

7.3.1.2.1 Additional Studies

These results are only the preliminary work in the fabrication and testing of nanostructured TiO₂ based resistive chemical sensors using NWs grown in a low oxygen environment. Currently this work is ongoing through collaboration with a group in the Department of Mechanical Engineering at the University of Malaya, Malaysia. They are investigating the sensitivity of the TiO₂ nanostructures grown on Ti64 particles to reducing environments including H₂ and CO. The main reason for the change in alloy from Ti5-5-5 to Ti64 has to do with availability. The Ti5-5-5 used in the previous discussion was produced in-house by atomization. This alloy is not commercially

available in powder form however, Ti64 is. They have successfully reproduced the growth of nanostructures on Ti64 particles using the process of oxidation in a low oxygen environment. Currently studies are being conducted to decrease the average particle size, optimize paste solution and composition including particle load, and binder burnout procedure to enhance thick film adhesion.

In parallel with the work being conducted in Malaysia an alternate approach to fabricating sensors using a nanostructured TiO₂ thin film substrate is being investigated in our laboratory. In this study, a thin film of Ti alloy would be directly deposited onto a sensing platform such as the Al₂O₃ substrate containing interdigitated Au electrodes by DC magnetron sputtering. The thin film would then be oxidized to produce NWs. The main advantage of the thin film sensor vs. the particle based sensor would be the ability to completely oxidize the metal alloy such that no further oxidation would occur during sensor testing. Additionally, a shadow mask could be employed to deposit the thin film in such a manner as to create interdigitated electrodes out of the Ti alloy. If the film thickness is sufficient to allow the growth of NWs with lengths in the 10s of microns it may be possible to create NW to NW contact across the electrode gap. This would greatly enhance the sensing performance of the sensor. A schematic representation of the pattern thin film sensor is presented in **Figure 7.7**.

We have successfully deposited a β stabilized titanium alloy from a Ti5-5-5 target by DC magnetron sputtering. They as deposited films were oxidized at 700C in 17 ppm of oxygen to promote NW growth. Early results show great promise towards using these films as gas sensor platforms. Current studies are investigating the optimum parameters

for depositing the alloy thin film onto an interdigitated sensor platform. Once this process is optimized NW oxidation studies and sensing measure will be performed. This work is in its early stages but shows promise as a useful application for the TiO_2 NWs grown by oxidation of Ti alloys. However, significant challenges must be overcome to make this technology a reality. These include a reduction in the required sensing temperature, stabilization of the baseline resistance, and improved adhesion of the particle based thick film.

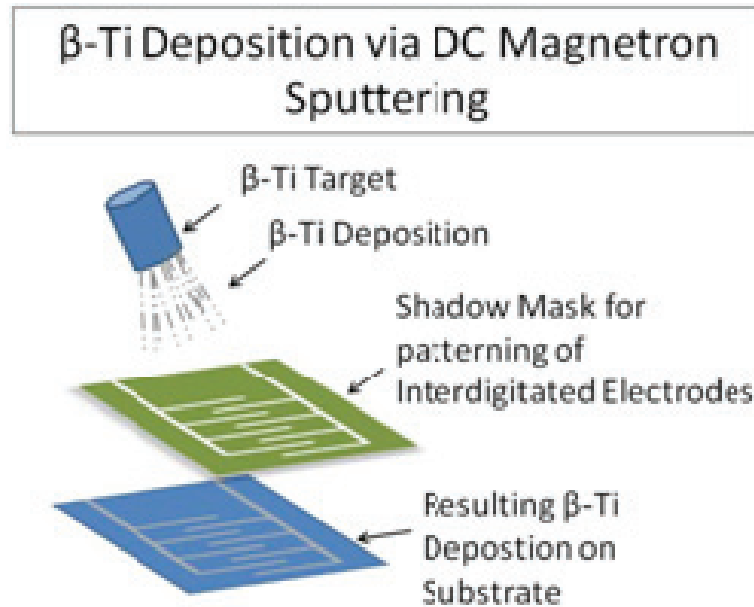


Figure 7.7: Schematic representation of a proposed thin film sensor being produced by DC magnetron sputtering.

7.3.2 Cell Adhesion Studies for Biomedical Implants – Ti64 Bulk

7.3.2.1 Background

Another application currently being pursued for the nanostructured TiO₂ growth on Ti alloys by simple oxidation is as surface coatings for biomedical implants to increase cell adhesion and proliferation. Ti and Ti64 have been widely used for biomedical applications as hip joint replacements and dental implants due to their mechanical and chemical stabilities and their biocompatibility.[34] However, the bioactivity of cells on Ti and Ti64 has been shown to be low which results in a reduced rate of cell adhesion and growth implants.[34] Surface modifications of the Ti based implants have been shown to enhance the bioactivity of cells by increasing the surface area.[35] There have been reports of direct depositions of coatings such as TiO₂ and hydroxyapatite (HA) on Ti or Ti64 plates to improve the bioactivity.[35] However, HA coatings are reported to have poor adhesion to the metal as well as poor mechanical stability in the body.[192] As an alternative, TiO₂ coatings deposited by thermal spray methods have been employed to increase the surface area of the implants. [193]

Previous work by Lee and Gallego-Perez investigated the use thermal spray TiO₂ coatings to increase cell adhesion on Ti64.[175] It is known that enhanced surface area can be beneficial in improving the bioactivity of cells. Thus, an attempt was made to modify the surface of thermal spray TiO₂ coated Ti64 samples with nanostructured growth.[176, 193, 194] They had limited success with this process but it required the initial step of applying the spray coating of TiO₂ to the implants prior to nanostructured growth. After Lee's graduation from OSU, I continued the collaboration with Perez investigating the influence of nanostructured growth on Ti64 on cell adhesion and

proliferation. Ti64 samples were oxidized directly without prior spray coating of TiO₂. For this study three sample sets were chosen: 1) Polished Ti64, oxidized Ti64 without nanostructured growth, and 3) Ti64 oxidized to produce an abundant coverage of TiO₂ NWs.

7.3.2.2 *Experimental*

Oxidation of the Ti64 samples was conducted in the same manner as reported in previous chapters. To produce both TiO₂ oxide films with and without NWs the Ti64 samples were oxidized at 700°C and 550°C, respectively. Oxide surface morphologies, cell adhesion, cell spreading, and cell morphology were studied via FEG-SEM SEM (Model Sirion, FEI, Oregon). The cells were first dehydrated in graded ethanol solutions (70, 80, 90, and 100%) and hexamethyldisilazane.

Cell response studies were conducted using human osteosarcoma (HOS) cells (ATCC, USA). Samples were first sterilized by autoclaving before being seeded with the HOS cells at a density of 5×10^4 cells/cm². Cells were cultured for 15 hours, 10, 25, and 35 days to test cell adhesion and proliferation. Alkaline phosphatase (ALP) activity, an early marker of bone differentiation, was evaluated at each time point by mixing an aliquot of culture medium with p-nitrophenyl phosphate (Sigma) at a 1:1 (vol/vol) ratio, and monitoring light absorbance of the mixture at 405 nm overtime.[195] ALP activity was calculated from the slope of the absorbance versus time curve. Cell proliferation was characterized after 15 hours via fluorescence microscopy and laser scanning cytometry (LSC).[196] The cells were fixed with a 2.5% glutaraldehyde solution in PBS, and the nuclei stained with PIRNase (BD Biosciences, California). A One-way ANOVA and a T-

Test were used to identify significant differences in cell proliferation and ALP activity ($\alpha= 0.05$).

7.3.2.3 *Results*

Figure 7.8 shows SEM images of the surface morphologies of the oxidized Ti64 samples prior to the introduction of HOS cells. The sample oxidized at 550C (**Fig. 6.8 A**) contains no NW growth, only an oxide layer. The samples oxidized at 700°C show an abundance of NW growth. SEM and fluorescence microscopy observations showed that once deposited, the cells were able to adhere, spread and proliferate on all three substrates (Ti64, TiO₂, and TiO₂ NWs). **Figure 7.9** shows fluorescence microscopy images of the nuclei of HOS cells after 15 hours of culture. The cells formed a relatively dense monolayer on the surface of each sample. Little variation in the number of cells on each of the different samples was observed after 15 hours of culture. SEM micrographs (**Fig. 7.10 A-C**) at 15 hours did not reveal significant differences in cell morphology between control (Ti64 and TiO₂) and nanotextured TiO₂ surfaces. The cells presented a star-like shape, exhibiting in some cases large cytoplasmic projections and in others, a uniform radial spreading. HOS cells on TiO₂ NWs showed abundant filopodia (micro spikes) interacting with the surface as noted by the arrows in **Figure 7.10 D**. After 10 days of culture the cells covered the entire surface of all the substrates. Long-term cultures ($t > 10$ days) showed signs of extracellular matrix deposition, and the cells began to exhibit a polygonal-like morphology (**Fig. 7.11 A-C**) which is typical of more mature osteoblasts.[197] Although this morphology was found on all the substrates, it tended to be more abundant and defined on the NWs.

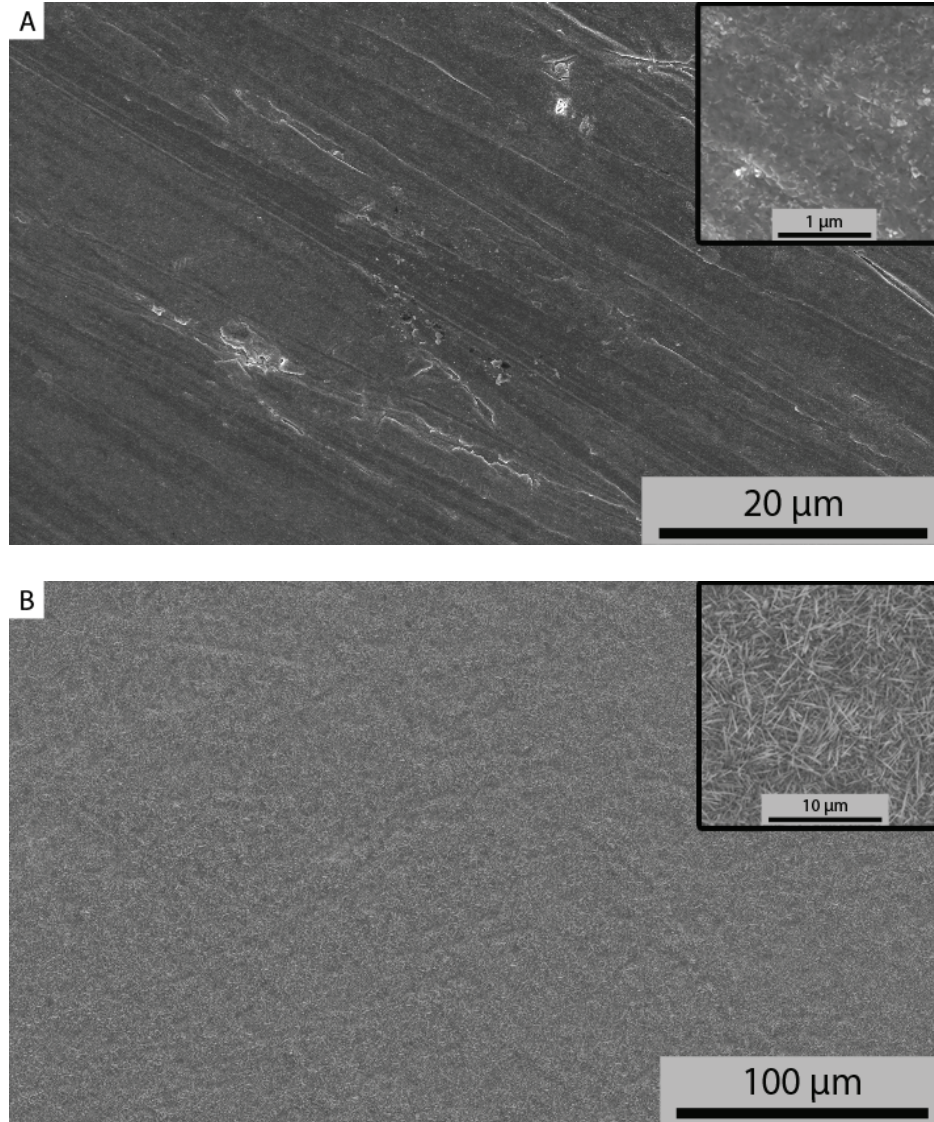


Figure 7.8: SEM micrographs of oxidized Ti64 substrates to produce A) TiO_2 film and B) TiO_2 NW coated surfaces for cell adhesion studies. Insets show higher magnification images of surfaces.

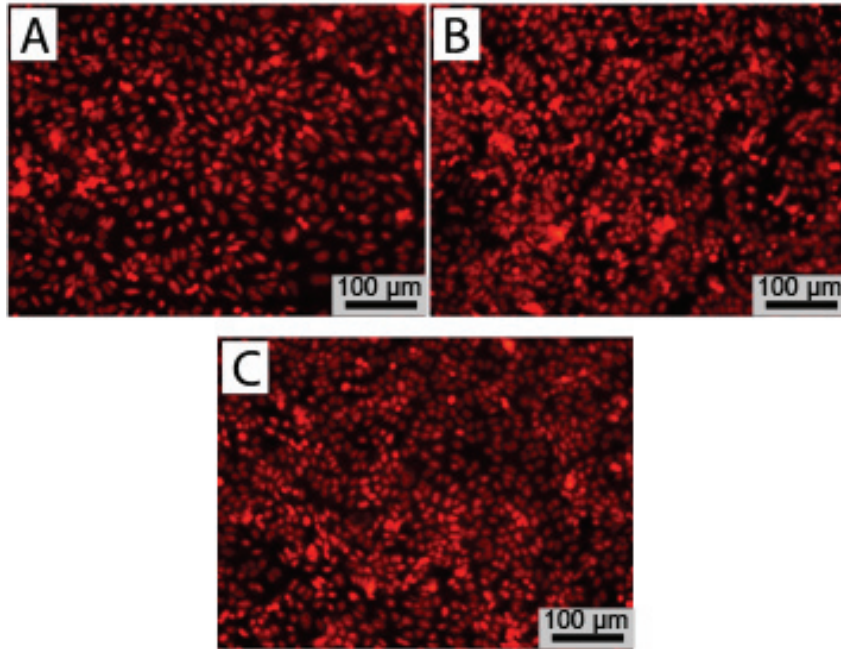


Figure 7.9: Fluorescence microscopy images of HOS cells (nuclei stained red) grown on A) Ti64, B) TiO₂ film and C) TiO₂ NWs for 15 hours.

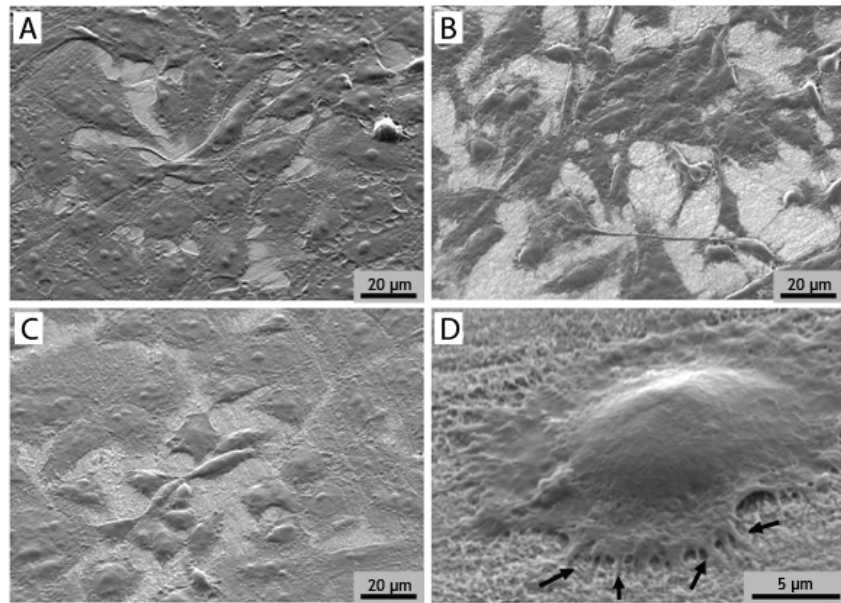


Figure 7.10: SEM images of HOS cells grown on A) Ti64, B) TiO₂ and C) & D) TiO₂ NWs for 15 hours. Cells on TiO₂ nanowires exhibited strong interactions with the substrate (black arrows).

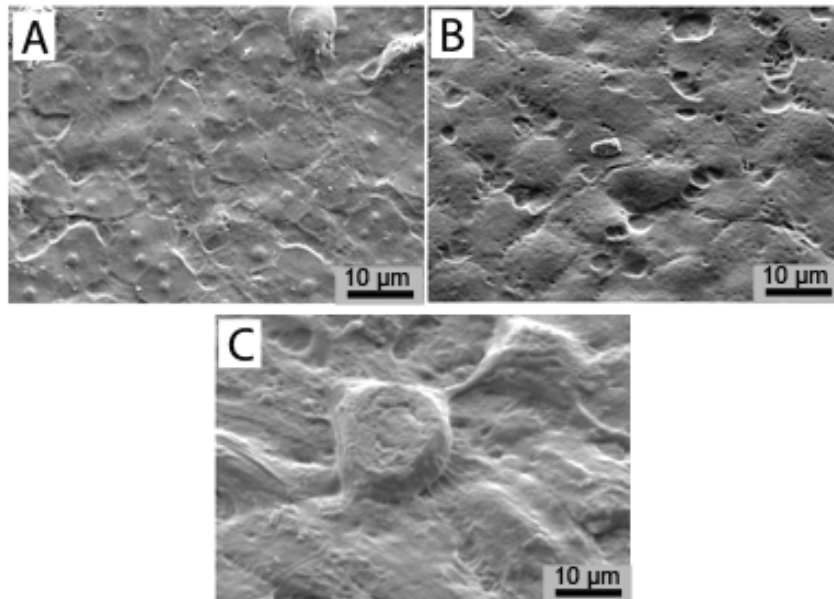


Figure 7.11: SEM images of HOS cells grown on A) Ti64, B) TiO₂ and C) TiO₂ NWs for 35 days. The cells exhibited a polygonal-like morphology.

LSC characterization (**Fig 7.12**) revealed an early increase in osteoblast-like cell proliferation on TiO₂ NWs, compared to flat Ti64 and TiO₂ substrates after 15 hours. There have been reports which indicate that nanotextured Ti-based surfaces upregulate the expression of specific bone proteins such as Osteopontin (OPN), Osteocalcin (OCN) and Bone Sialoprotein (BSP).^[36, 198, 199] De Oliveira and Nanci reported early expression of BSP and OPN by osteoblasts cultured on nanostructured Ti surfaces.^[36] BSP and OPN are known to contain adhesion-promoting peptide sequences (e.g. RGD), which are believed to trigger important cellular processes, including adhesion, proliferation, differentiation and migration.^[200-202] Further studies are required to

investigate what role, if any, BSP and OPN play in the increased proliferation observed on the TiO₂ NW samples.

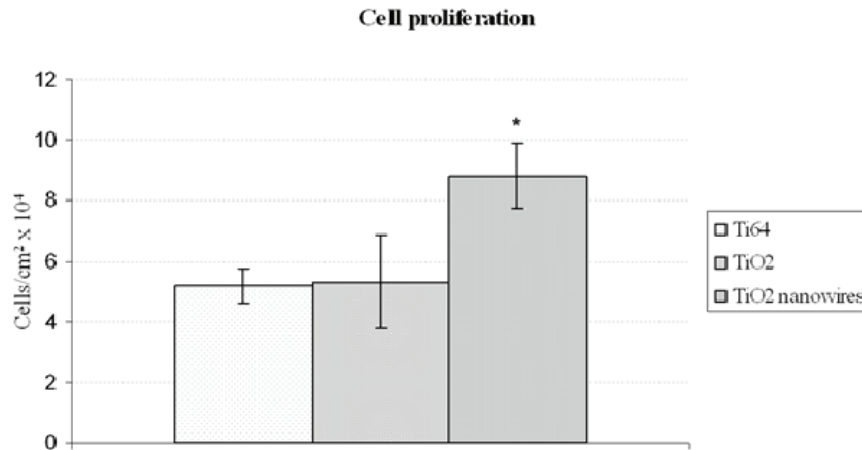


Figure 7.12: Osteoblast-like cell proliferation after 15 hours (“*” indicates statistically significant difference).

It was also found that osteoblast-like cells exhibited increased ALP activity (Fig. 7.13) after 15 hours and 10 days of culture on TiO₂ NWs, with respect to flat Ti64 and TiO₂ substrates. ALP activity has been widely recognized as a marker for bone cell functionality.[195, 203] Expression levels are usually elevated during dynamic extracellular matrix deposition.[204] ALP activity on flat Ti64 and TiO₂ remained relatively constant at any given time point.

TiO₂ NW coated Ti64 samples showed increased cell adhesion and proliferation compared to the non-nanostructured TiO₂ and bare Ti64 substrates. The increased cell growth is attributed to the NWs enhancing the growth of the extra cellular matrix. The next steps for this work are to investigate how actual bone cells will react to the

nanostructured surfaces. An additional collaboration is being formed with OSU's dental school to look at the feasibility of using this surface treatment with Ti based dental implants. This would be a parallel study to the work outlined here that may allow for a broader application of this nanostructured coating process for biomedical applications.

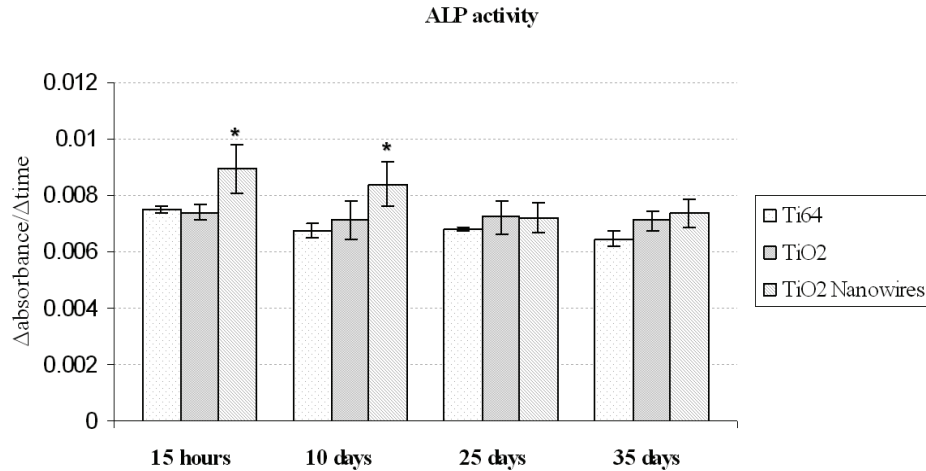


Figure 7.13: ALP activity of osteoblast-like cells grown on Ti-based substrates (“*” indicates statistically significant difference).

7.3.3 Ultra-short and Intense X-ray Sources – Ti64 Foil

7.3.3.1 Background

Recent advances in the field of intense short pulse lasers have revealed new opportunities for discoveries in physics and other related disciplines such as chemistry, biology and material sciences.[205, 206] Laser pulses with duration on the order of femtoseconds (10^{-15} s) can deliver extremely high intensities (10^{15} - 10^{22} W/cm²) when focused onto a target with a typical focal spot diameter of a few microns. At such high intensities atoms comprising the target will be ionized in a time much shorter than one optical cycle.[207]

In a real laser system, the laser pulse is preceded by a low intensity pedestal called prepulse, which is caused mainly by amplified spontaneous emission (ASE). Typical ASE prepulse for an fs-class laser can be several ns long and have a contrast ratio of 10^{-4} to 10^{-7} by intensity. Given the peak intensity of around 10^{15} - 10^{20} W/cm², the prepulse of such laser system has sufficient energy to ionize matter.[206] The prepulse will interact with the target before the main pulse creating a layer of plasma with gradually varying density in front of it, referred to as preplasma. When the main pulse arrives, it interacts with the preplasma and not the initially sharp target interface. Shape of the preplasma (density profile) changes how the laser energy is coupled to the plasma electrons. During the interaction with the preplasma, the main laser pulse will transfer part of its energy to the target. Since electrons are much lighter than ions, the majority of this energy transfer occurs between the laser and the plasma electrons. A very large number of electrons are accelerated by the laser to very high energies (MeV and above) by different mechanisms and then pushed into the target. Depending on the laser intensity and preplasma density profile, various laser absorption mechanisms will dominate.[207] For example, the vacuum heating mechanism is effective for p-polarized light and the $\mathbf{J} \times \mathbf{B}$ mechanism dominates if the laser intensity is large enough. While streaming through the target, those energetic electrons accelerated by the laser create broadband bremsstrahlung radiation by colliding with the background nuclei and very narrow $K\alpha$ emission line by knocking out the inner shell (K-shell) electrons thus creating a vacancy which is then filled by an electron from the next shell (L-shell) followed by the emission of a photon with a characteristic energy. $K\alpha$ emission is approximately monochromatic and isotropic while

bremsstrahlung radiation is very broad, weaker than $K\alpha$, although more directional (peaked along the laser k-vector).[186] **Figure 7.14** shows a typical X-ray spectrum for a copper wire target. A bright $K\alpha$ line (8 keV for Cu) is clearly visible above the bremsstrahlung signal.

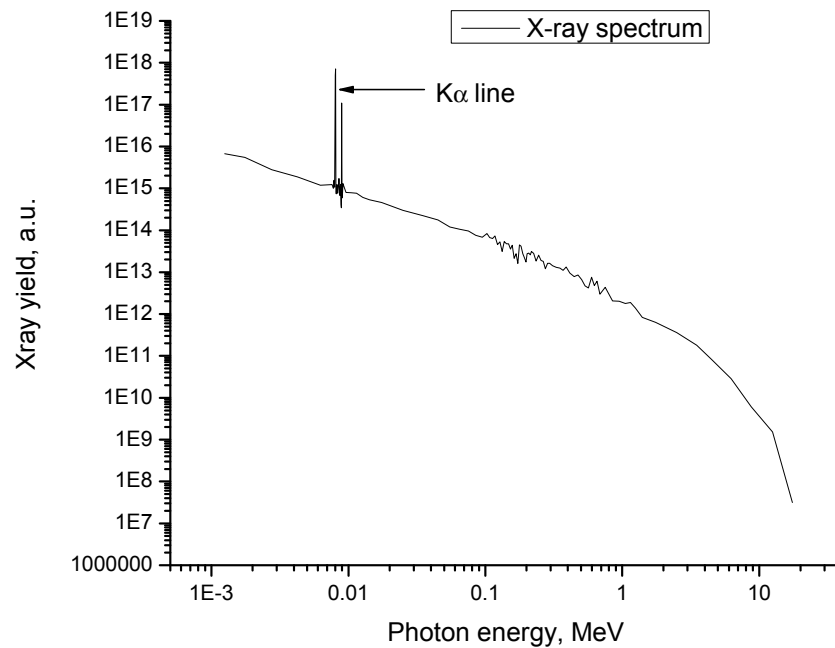


Figure 7.14: X-ray spectrum for a copper NW target.

The target surface can greatly affect the laser-to-electron coupling efficiency and increase the X-ray yield.[208] Targets with nanostructured surfaces have the potential of efficiently providing high X-ray yields. It is a well-known fact that geometric singularities such as sharp needle points can give rise to extremely high electric field (“lightning rod” effect). Such enhancement of electric field can increase the coupling of

the laser to the plasma thus increasing the X-ray yield. Moreover, the presence of geometric singularities on the target surface increases the effective area of the interaction with the laser which can further increase the energy conversion and the X-ray yield. Several groups have reported the enhancement of the X-ray signal when rough surface targets were used instead of the flat foil targets. These experiments used laser intensities between 10^{15} - 10^{17} W/cm². [205, 206, 208] High X-ray yields can also be achieved from rough surface structures such as nano-wire targets. In this case, only a high-contrast laser can be used as even a small prepulse will destroy the nano-structures. [186]

7.3.3.2 *Experimental*

Nanostructured targets were grown on 4"x2.5"x0.018" Ti64 foils by oxidation in a controlled atmosphere. The Ti64 samples were cut from a larger 0.018" thick sheet by an electric discharge machine (EDM). To oxidize the samples, Ar gas was introduced only after the furnace ramp to 700°C had begun. This resulted in an initial oxygen environment of near ambient levels. The concentration then decreased until it was equaled to that of the incoming gas. Using this oxidation method Ti64 samples were completely covered in TiO₂ NWs as observed in **Figure 7.15**. For the laser studies, a Red Dragon laser housed at Wright Patterson Air Force Base (WPAFB) capable of producing peak intensities on the order of 10^{15} W/cm² was used. The laser had a relatively small prepulse with a typical contrast of 10^5 . Samples were fixed in a mounting jig to hold them flat while the laser was rastered across their surface.

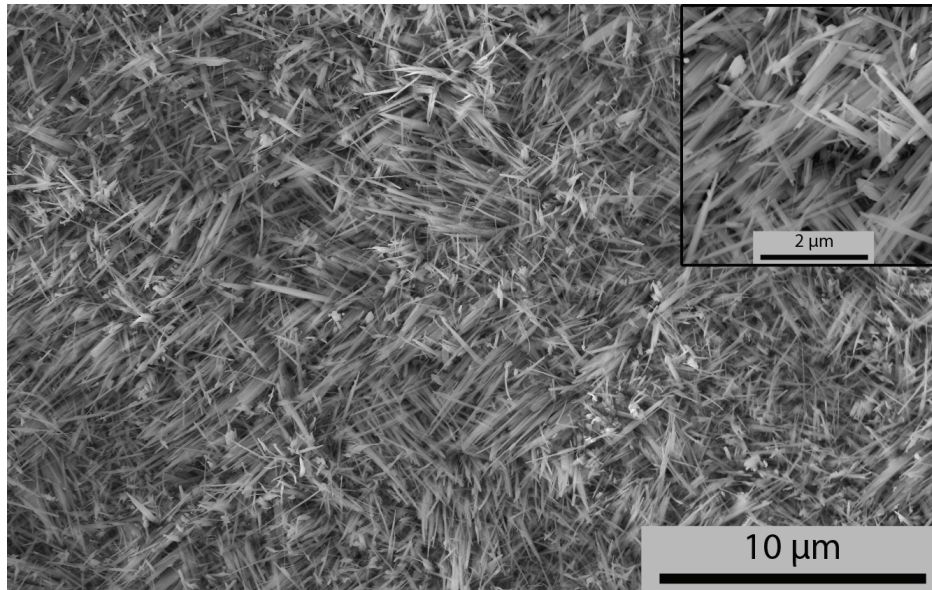


Figure 7.15: SEM image of NW growth resulting from the oxidation of Ti64 foil at 700°C for 8 hours with a initial ambient oxygen levels decreasing to 10 ppm over time. Inset shows higher magnification of wires.

7.3.3.3 *Results*

Initially, this ultra short and intense x-ray study was being conducted on nanostructured copper oxide targets. However, the nanostructured oxide films formed on the Cu substrates by oxidation in air proved to be weakly bonded to the Cu surface causing them to delaminate and flake off. Thus, the nanostructured TiO₂ was used as an alternative. It should be noted that this work is in its infancy and only a small number of TiO₂ NW samples have been tested for X-ray emission. The majority of the work to date has been focused on the optimization of NW growth on large area Ti64 foil samples. Several challenges were encountered when scaling up the oxidation process for the large samples required for the X-ray emission tests. The following discussion highlights some of these

challenges and the means by which they were overcome. Preliminary results for the X-ray emission studies are presented as well.

7.3.3.3.1 Optimization for Large Ti-6AL-4V Targets

Initial NW growth tests on the supplied Ti64 targets proved very promising and a procedure was quickly developed to produce complete coverage on the Ti alloy surface (**Fig. 7.15**). However, oxidation of larger Ti64 targets did not result in NW growth. Until this study, the average sample size used in the NW growth studies on Ti alloy substrates was 0.8"x0.8"x0.04". When a sample as large as 2"x1.25"x0.018" was oxidized no NW growth was observed. The reason for this became evident very quickly. **Figure 7.16** shows the oxygen profile (solid line) during oxidation for a 0.8"x0.8"x0.04" Ti64 sample oxidized in 40 ppm of oxygen. As the furnace temperature ramps, a decrease in the oxygen environment can be observed. This corresponds to the rate at which oxidation took place on the metal. Eventually the oxygen consumption decreased and remained at a rate of approximately 2 ppm until the furnace began to cool. This shape of the oxygen profile was observed time and again in samples where NW growth occurred. However, in these tests, the oxygen concentration was held constant prior to the ramping of the furnace such that the oxygen concentration was fixed for the duration of the experiment. For oxidation tests from ambient oxygen concentration this was not the case. Instead a decreasing oxygen concentration was observed for the first 3-4 hours of oxidation.

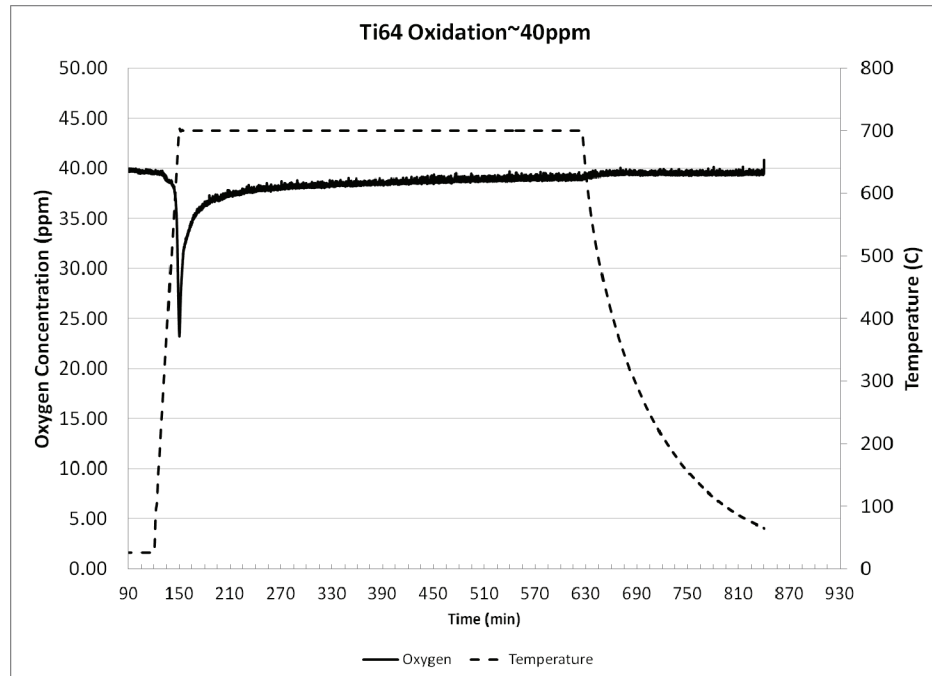


Figure 7.16: Oxygen profile vs. oxidation time for a 0.8”x0.8”x0.04” Ti64 sample oxidized at 700°C for 8 hours at 40 ppm O₂.

Figure 7.17 shows an SEM image and corresponding oxygen profile for a 1.25”x0.5” Ti64 foil oxidized at 700°C for 8 hours from ambient oxygen environment. The oxygen sensor output was scaled from 0 – 250 ppm such that the detail of the low oxygen regime could be captured. Unfortunately, this resulted in a loss of data for all oxygen concentrations above 250 ppm as seen in the flat region at the start of the plot in **Figure 7.17 B**. An abundance of NW growth was observed on the surface of the sample (**Fig. 7.17 A**) resulting from this oxidation process. The oxygen profile during this oxidation experiment was observed to drop rapidly reaching a low of approximately 8 ppm after which it climbed slightly stabilizing near 10 ppm for the duration of the oxidation process. This behavior is similar to that observed in the constant oxygen environment

oxidation tests. However, the oxygen profile for the larger samples did not have this same behavior.

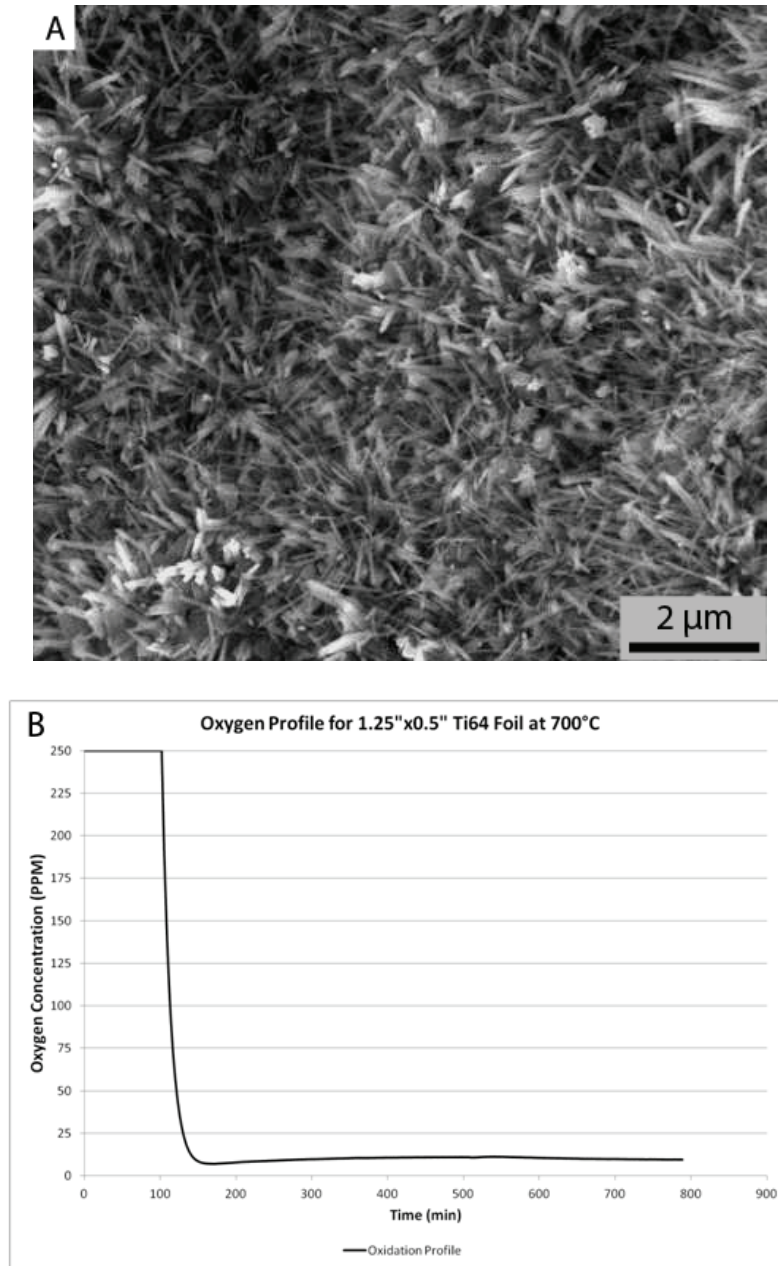


Figure 7.17: A) SEM image showing NW growth on a 1.25''x0.5'' Ti64 foil sample oxidized at 700C for 8 hours in a decreasing oxygen environment. B) The corresponding oxygen environment during oxidation.

A larger Ti64 foil sample (4"x2.5") was oxidized using the same procedure as outlined above for the 1.25"x0.5" sample. The resulting surface morphology and oxygen profile are shown in **Figure 7.18**. This sample did not produce NWs but rather pillar type structures. These poor results can be interpreted with the help of the oxidation profile for this experiment (**Fig. 7.18 B**). Again, a rapid drop in oxygen concentration similar to that for the smaller Ti64 foil sample was observed however this time, a steady oxygen concentration is not attained. Instead a bottoming out of the oxygen concentration was observed. That is, the oxygen concentration in the reaction chamber is below the measurable limit for the oxygen sensor. A sharp increase in the oxygen concentration is observed 510 minutes into the experiment corresponding with the turning off of the furnace (30 minute ramp + 480 minute anneal). As the furnace cools the oxidation rate is reduced corresponding to a lowering of the oxygen consumption by the Ti sample. Only a slight increase in the oxygen concentration was observed at 510 minutes for the smaller Ti64 foil sample as the oxygen concentration was already near the background level. In the case of the larger sample, the increased oxygen consumption can be attributed to the increase in exposed Ti64 area (10 in² vs. 0.625 in²).

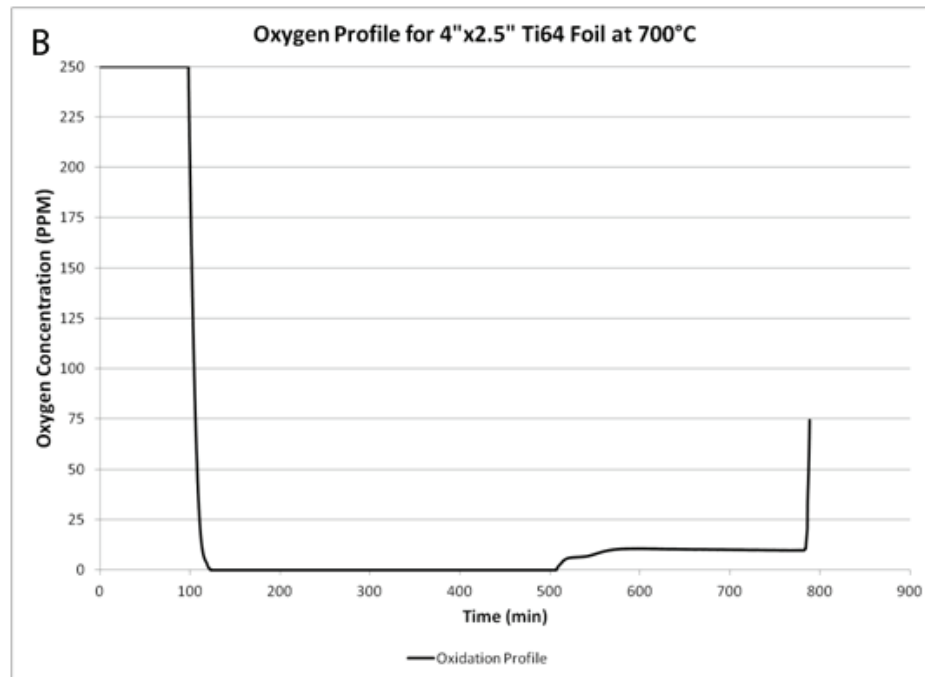
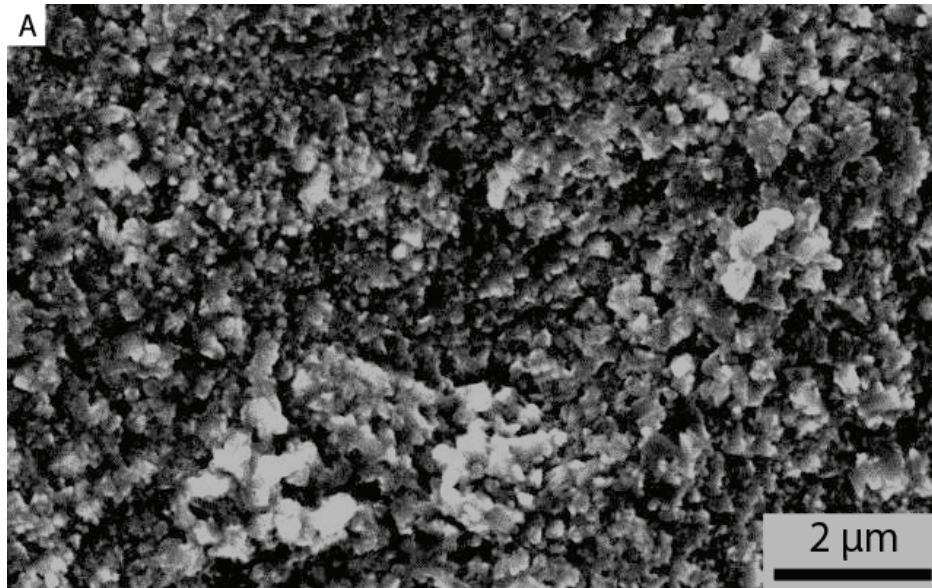


Figure 7.18: SEM image showing NW growth on a 4''x2.5'' Ti64 foil sample oxidized at 700°C for 8 hours in a decreasing oxygen environment. B) The corresponding oxygen environment during oxidation.

The rate of oxygen consumption per in^2 can be obtained by computing the total oxygen consumed for a given sample and dividing it by the sample area. This calculation is only applicable to samples where the complete oxygen profile is known. For samples oxidized in an environment starting at or near ambient oxygen concentrations the oxygen profile is ambiguous at early times and cannot be directly used to calculate oxygen consumption. Taking for example the oxygen profile in **Figure 7.16**, the oxygen consumed is easily calculated because the oxygen concentration entering the reaction chamber is constant and known. Thus a simple subtraction of the measured oxygen concentration from that of the baseline concentration would yield the amount of oxygen being consumed at each data point. Once the oxygen consumption at each data point is known, one can either sum this information over all data points to obtain the total amount of oxygen consumed or, take the average consumption over all data points and divide it by the rate of data collection to obtain an average rate of oxygen consumption. Either of these values can then be divided by the sample area to obtain a predictive value for the amount of oxygen consumed per in^2 either as a total amount or a rate.

This method was applied to a number of samples oxidized at known oxygen baseline levels and was shown to be relatively accurate at predicting the amount of oxygen consumed for a given sample size. It was then applied to the samples oxidized with a changing oxygen baseline, i.e. oxidation starting from ambient concentration. It was necessary to use the rate of oxygen consumed per in^2 for the changing baseline samples as the total amount consumed was impossible to measure. Doing so enabled the calculation of the required flow of oxygen into the reaction chamber throughout the

oxidation experiment. For example, a flow of 10 ppm for the 1.25"x0.5" Ti64 foil sample was sufficient to allow the sample to fully oxidize without consuming all of the oxygen being supplied however this was insufficient for the 4"x2.5" sample. Using the rate of oxygen consumption to be $\sim 5.3 \text{ ppm in}^{-2} \text{ min}^{-1}$ (as calculated from constant background experiments), the calculated minimum oxygen concentration for the 1.25"x0.5" sample would be only $\sim 2.7 \text{ ppm/min}$ while that of the 4"x2.5" would be $\sim 43 \text{ ppm/min}$. Thus, an oxygen flow rate of 10 ppm/min would supply sufficient oxygen for NW growth on the 1.25"x0.5" sample but not the 4"x2.5" sample. However, increasing the oxygen concentration being flown into the reaction chamber to a level above 43 ppm would keep the 4"x2.5" Ti64 foil from getting all of the oxygen in the chamber and should promote NW growth.

Recent results using this calculation method for predicting the required oxygen concentration have proven successful as shown in the SEM images in **Figure 7.19**. Reproducibility studies are underway in parallel with early x-ray emission studies. However, the preliminary results are not yet available. Work is continuing on this research effort through collaboration between our group members and our counter parts in both the Department of Physics here at OSU and at WPAFB.

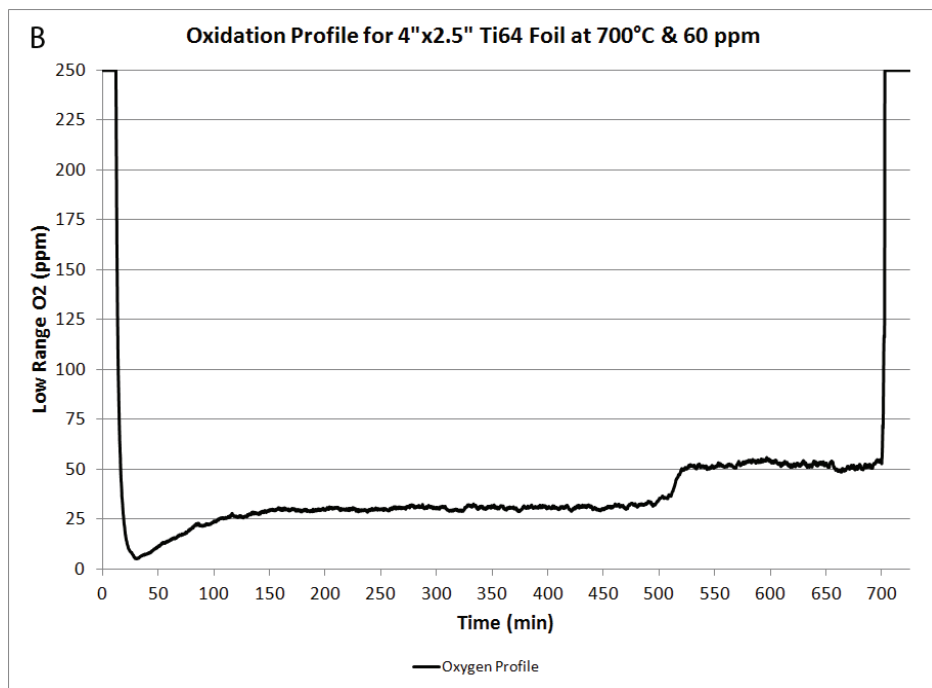
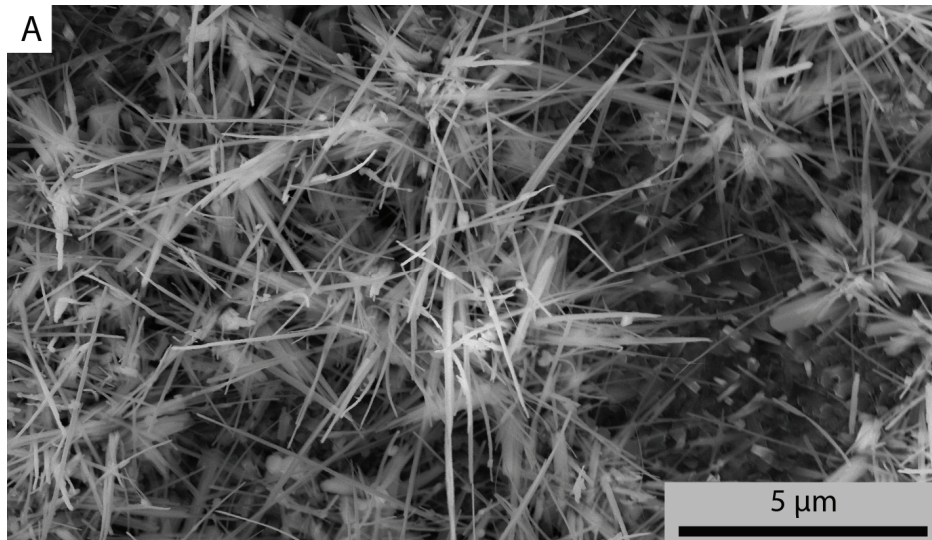


Figure 7.19: A) SEM image showing NW growth on a 4''x2.5'' Ti64 foil sample at 700°C for 8 hours in a decreasing oxygen environment with a minimum concentration of 60 ppm. B) The corresponding oxygen environment during oxidation.

7.3.4 Hydrothermal Conversion to Dendritic BaTiO₃ – CPTi Foils

7.3.4.1 Background

While conducting research on the impact of various growth parameters on the production of NWs from the oxidation of CPTi in a humid environment, a collaboration was developed with Dr. Ed Herderick who was simultaneously conducting research involving the hydrothermal conversion of TiO₂ metal-oxide-metal (MOM) NWs to barium titanate.[25] We combined our processes, oxidation to produce TiO₂ NWs and hydrothermal conversion to produce BaTiO₃, and discovered a rather unique morphology; dendritic barium titanate. Prior to this work, almost no mention of BaTiO₃ dendrites were reported in the literature. As such, this structure was a singularity worthy of further research.

What makes BaTiO₃ such an interesting material is that it exhibits ferroelectric and piezoelectric behavior at room temperature. It also has an extremely high dielectric constant. It has been used in a range of applications including RAM, dielectric gates, ceramic capacitors and in nonlinear optics.[209, 210] Typically, nanoparticles, nanowires, nanorods, and nanotubes are produced by hydrothermal conversion of a TiO₂ powder with a barium precursor in an autoclave. We utilized the same approach however the TiO₂ nanostructures on a CPTi foil were used for the TiO₂ source. Dendritic and rectangular structures of BaTiO₃ were observed after the conversion of the nanostructured precursor. The following sections present a discussion of the different BaTiO₃ morphologies observed as well as a preliminary investigation of the ferroelectric properties.

7.3.4.2 *Experimental*

Nanostructured TiO₂ samples were grown on CPTi foils using the procedure outlined in Chapter 6. Briefly, foil samples were placed in a horizontal tube furnace and annealed at 700°C for 4 hours under flowing Ar bubbled through DI water. As-grown samples were characterized via SEM prior to hydrothermal treatment. As the samples were to be used for further processing no Au coating was used to prepare the samples for SEM analysis. Instead, a clip style SEM mount was used to allow sufficient electron flow from the samples to prevent charging during imaging.

Hydrothermal conversion was carried out in a Teflon lined stainless steel acid digestion bomb (Parr Instrument Company, 276AC2-T304). A 0.1M Ba(OH)₂ solution was prepared from either Ba(OH)₂-H₂O (≥98%,Sigma Aldrich) or Ba(OH)₂-8H₂O (≥98%,Sigma Aldrich) and DI water. The DI water was boiled for 30 minutes prior to the addition of the Ba(OH)₂ precursor to remove CO/CO₂ content from the water. The solution was stirred for 10 min. During this time the nanostructured TiO₂ sample was placed in a Teflon holder to suspend it above the bottom of the Teflon lined stainless steel pressure vessel. Then, the 0.1M Ba(OH)₂ solution was added to the pressure vessel until it was 70% full. The pressure vessel was then sealed and placed in an oven (Lindberg, 601320A-1) to heat it to the desired conversion temperature (180-220°C). The hydrothermal conversion was allowed to proceed for several hours at this elevated temperature. After which, the pressure vessel was removed from the oven and allowed to cool to room temperature before opening. Once removed, the converted samples were rinsed in DI water for 5 min and dried in a vacuum oven (Lindberg, V0714C) to remove any residual material remaining from the conversion process.

The ferroelectric response of the dendritic barium titanate was performed on a Precision Pro Material Analyzer (Radiant Technologies) in conjunction with the Vision software suite. Early test were performed in Professor Tan Ooi Kiang's Sensors and Actuators Lab at Nanyang Technological University (NTU) in Singapore. A top electrode contact point having a diameter of 1 mm and thickness approximately 250 nm was deposited on the top surface of the converted foil by E-beam lithography. Silver paste was used to attach the sample to a Pt wafer forming the bottom electrode. The Ag paste was cured at 450°C in air to ensure a strong bond between the Pt wafer and converted foil. Electrical connections were made using a standard 4-point probe with hot chuck (Instec, MK1000). Polarization measurements were performed at frequencies of 500 Hz and 1 kHz and voltages between 0.5 V and 5 V. A qualitative Curie temperature investigation was performed using the heated stage of the 4-point probe by conducting hysteresis loop measurements at increasing temperatures. The temperature was allowed to stabilize for 1 hour prior to the start of the test to ensure a uniform sample temperature. The temperature of the actual sample was measured via an infrared thermometer.

7.3.4.3 Results

An SEM image of a typical nanostructured TiO₂ sample is observed in **Figure 7.20 A**. Since these nanostructured foils were capable of being imaged in the SEM without the need for Au coating, it was possible to image the nanostructure morphology prior to hydrothermal conversion. The sample in **Figure 7.20** was hydrothermally converted to barium titanate (BaTiO₃) using a 0.1M solution of Ba(OH)₂·8H₂O at a temperature of 210°C for 18 hours. The surface of the foil after hydrothermal conversion was covered in

dendritic structures microns in scale (**Fig. 7.20 B**). Energy dispersive spectroscopy (EDS) was performed on these structures in the SEM, but due to the overlap of the Ba $L_{\alpha 1}$ peak (5.47 keV) with the Ti $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks (5.51 keV and 5.5 keV respectively) it was not possible to distinguish the presence of barium from that of titanium. As such, X-ray diffraction (XRD) analysis was employed to investigate the structure of the converted samples. The results of this analysis showed a mixture of rutile TiO_2 (PDF# 65-0190) and BaTiO_3 (PDF# 05-0626) structures after conversion at 210°C for 20 hours as observed in **Figure 7.21**.

Additional hydrothermal conversions were performed on nanostructured CPTi substrates using a variety of conversion parameters. Typically the conversion temperature and duration were varied although a systematic investigation of these parameters has not yet been conducted. Currently, this work has been taken on by an incoming graduate student, who will conduct an exhaustive investigation of these and other hydrothermal conversion parameters. The following discussion highlights some of the different morphologies observed forming from the hydrothermal conversion of the nanostructured CPTi samples. Conversion and growth parameters are provided where available.

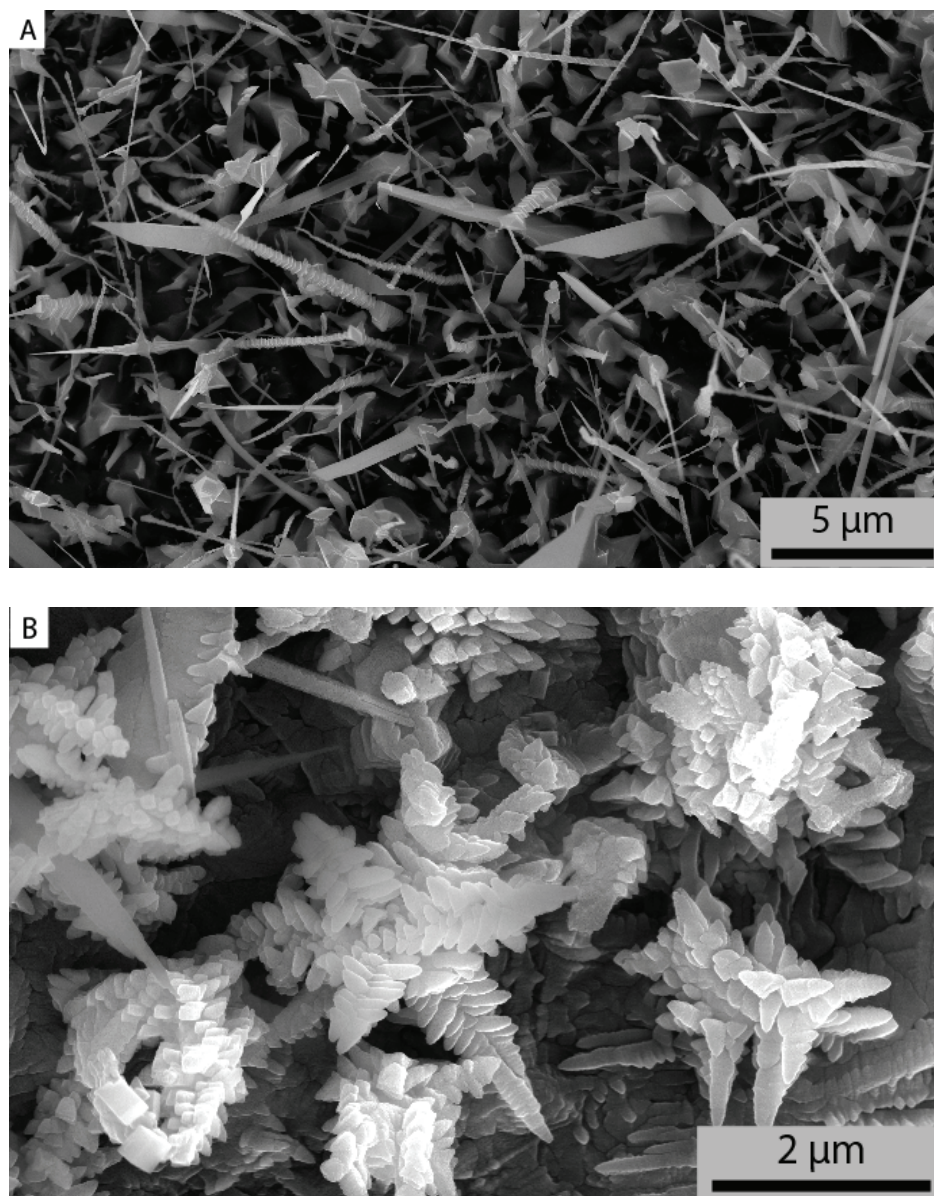


Figure 7.20: SEM images of nanostructured TiO_2 A) before and B) after hydrothermal conversion to form dendritic barium titanate.

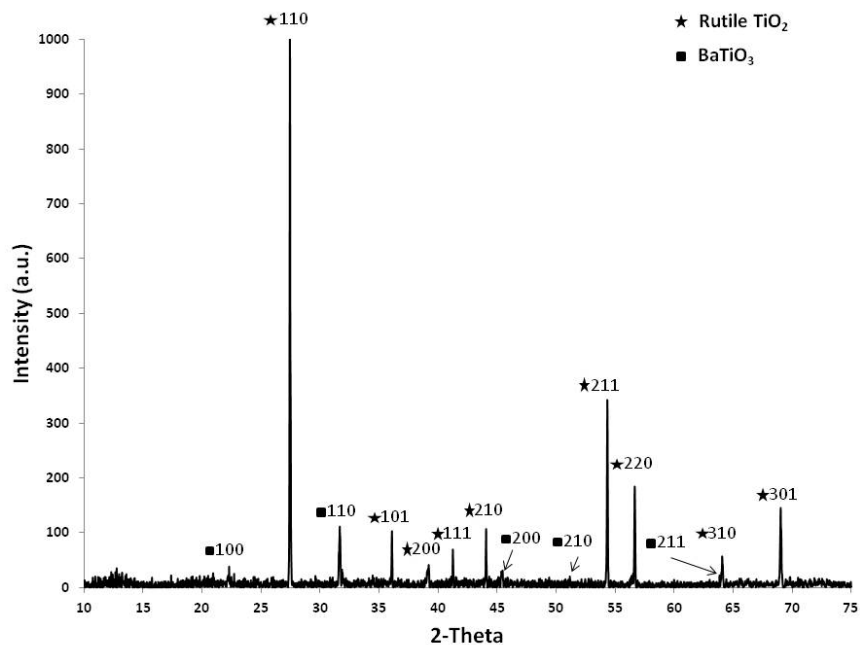


Figure 7.21: XRD spectra obtained from a converted sample showing both rutile TiO_2 (PDF# 65-0910) and BaTiO_3 (PDF# 05-0626) crystal structures.

Multiple morphologies were observed resulting from the hydrothermal conversion of nanostructured CPTi foils. Hydrothermal conversion at 210°C for 20 hours produced two distinct dendrite morphologies as well as rectangular shapes as can be observed in **Figure 7.22**. Both of the dendrite morphologies had similar characteristics with only slight variations in their overall shape. **Figure 7.22 B** shows one of the dendrites having a regular high symmetry morphology consisting of a main trunk with four rows of branches sticking out perpendicular from the sides of the trunk at what appears to be 90° angles to one another. Similar dendrite morphology is observed in **Figure 7.22 C** however in this morphology, several of the dendrite structures observed in **Figure 7.22 B** appear to be coming out of a central location. These appear to be two variations of the same

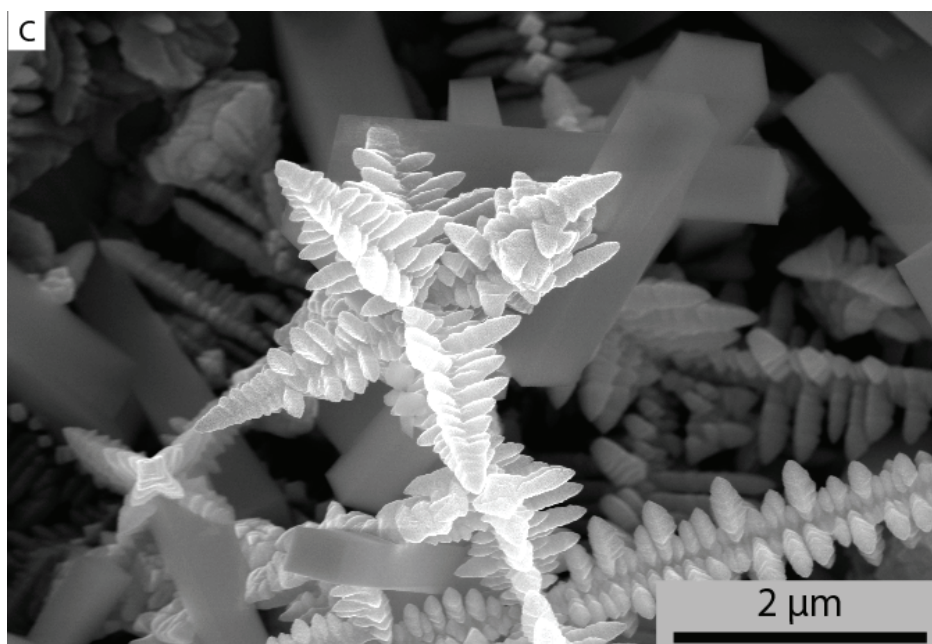
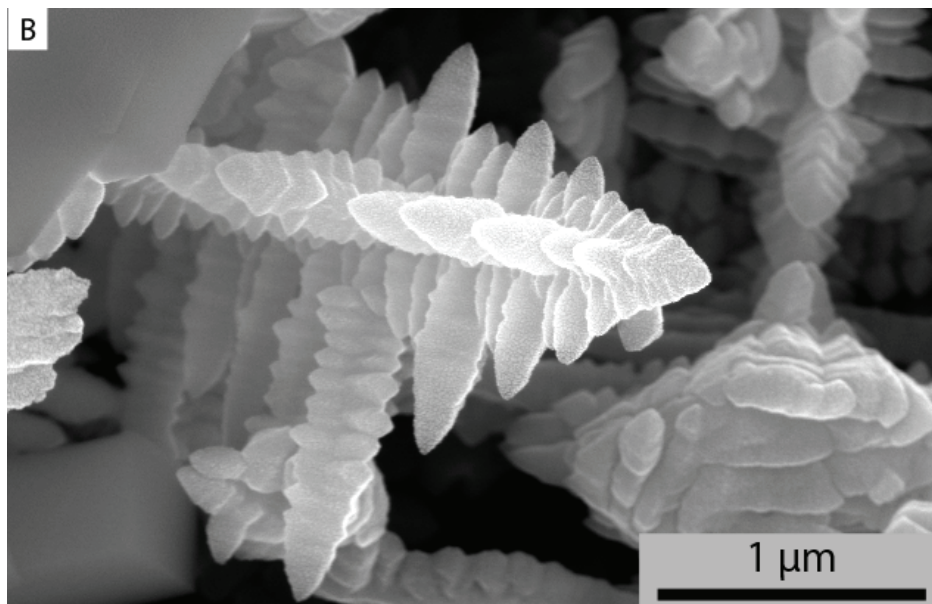
morphology but are worth noting independently. Both appear to exhibit high levels of symmetry. The third morphology observed in this sample was vastly different from the previously described dendrite structures. Elongated rectangles were observed intermixed with the dendrite morphology as observed in all images in **Figure 7.22**. They ranged in size from a few hundred nanometers to more than a micron in diameter with lengths in excess of 5 μm . In this sample, wherever dendrites were observed the rectangular morphology was also present however the reverse was not true. Large sections of the sample did not contain dendrites rather only the rectangular morphology as illustrated in **Figure 7.23**. What promotes the formation of one structure over another is not yet clear but is the topic of future investigations.



continued

Figure 7.22: SEM images of various structures observed resulting from hydrothermal conversion for 20 hours at 210°C in a 0.1M Ba(OH)₂ solution.

Figure 7.22: Continued



continued

Figure 7.22: Continued

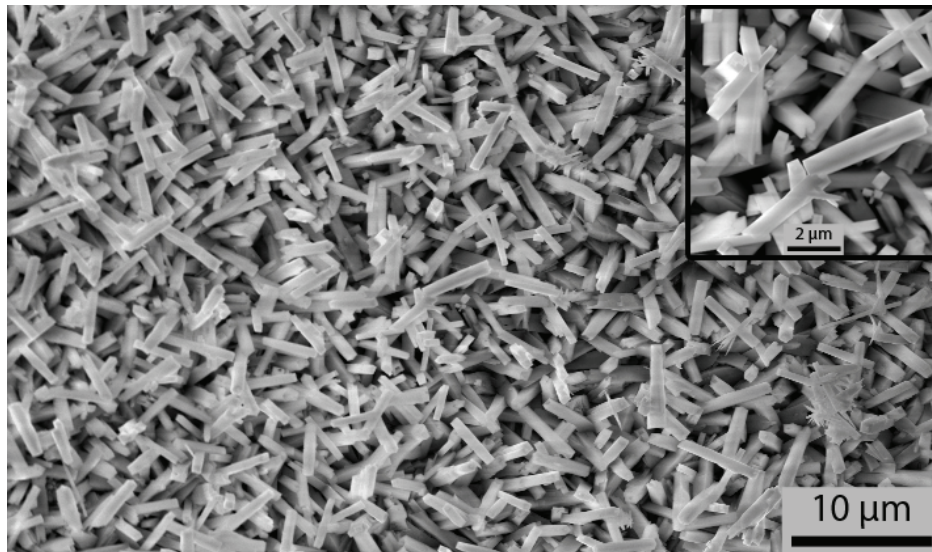
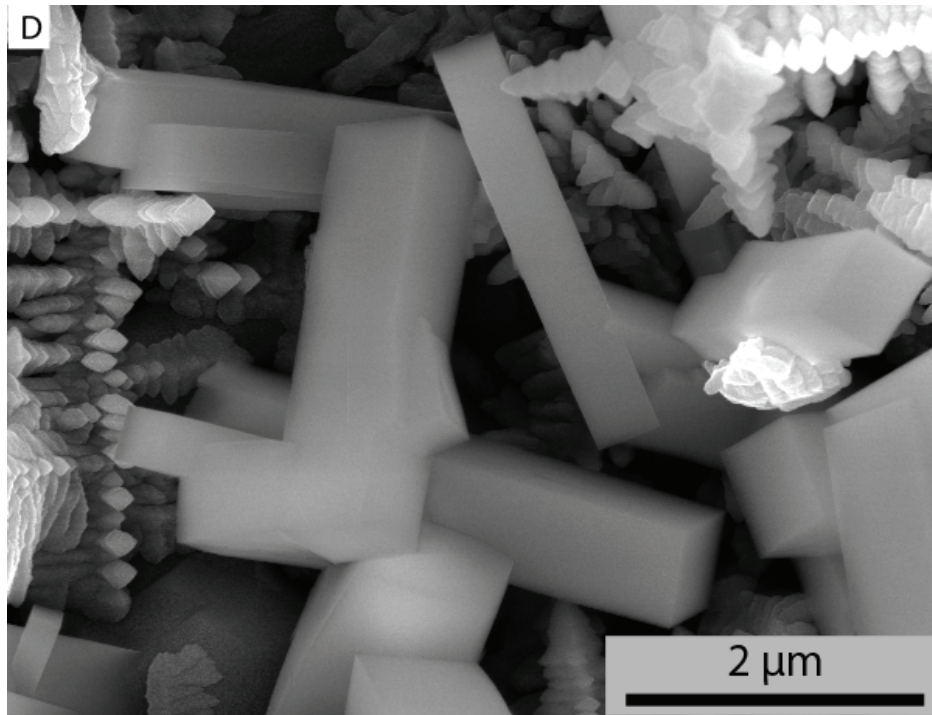


Figure 7.23: SEM images showing large areas of the converted sample containing only the rectangular structures. Inset shows higher magnification image.

A slight change in the conversion temperature can impact the resulting dendrite morphology. **Figure 7.24** shows the surface morphology pre and post hydrothermal conversion at 200°C for 20 hours. Under these conditions dendrites formed but with slightly different configurations from those in **Figure 7.22**. A temperature of 200°C also produced dendrites showing an apparent 4-fold symmetry but these dendrites had flat tops with four branches (**Fig. 7.25 A**). The previous dendrites exhibited either angled branches at their tops (**Fig. 7.22 C**) or a single point (**Fig. 7.22 B**). Angled branches were observed in the samples converted at 200°C however they appeared to only occur on dendrites with only three branches as observed in **Figure 7.25 B**. There is insufficient evidence at this time to conclude the changes in morphology observed at the lower conversion temperature are a direct result of this decrease. The nanostructured TiO₂ surface morphology used as the precursor to this conversion could also play an important role. Further studies are necessary to make this determination.

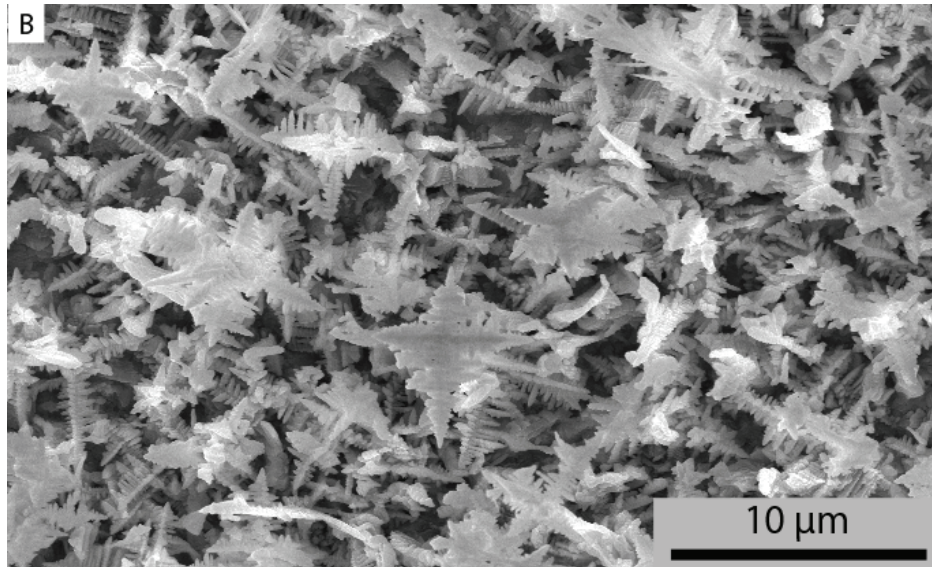
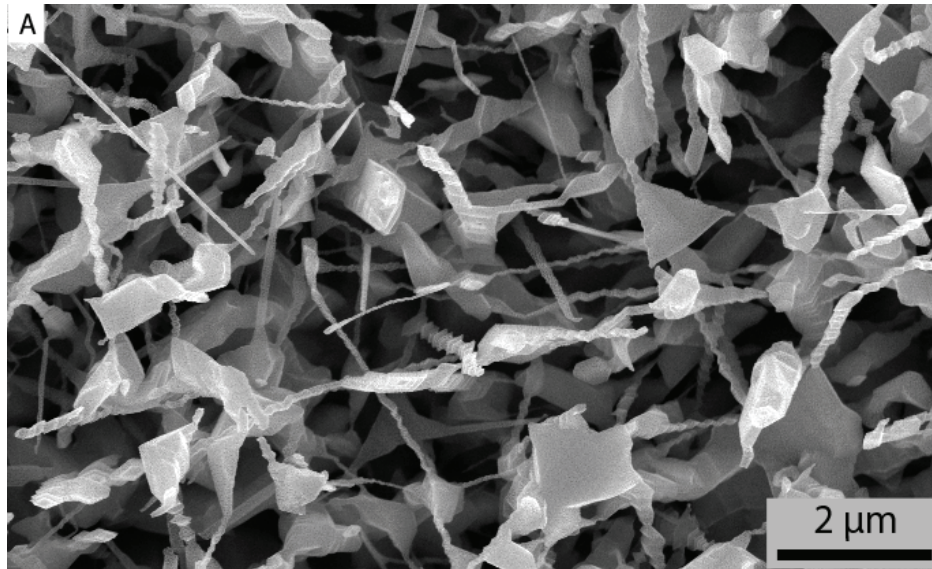
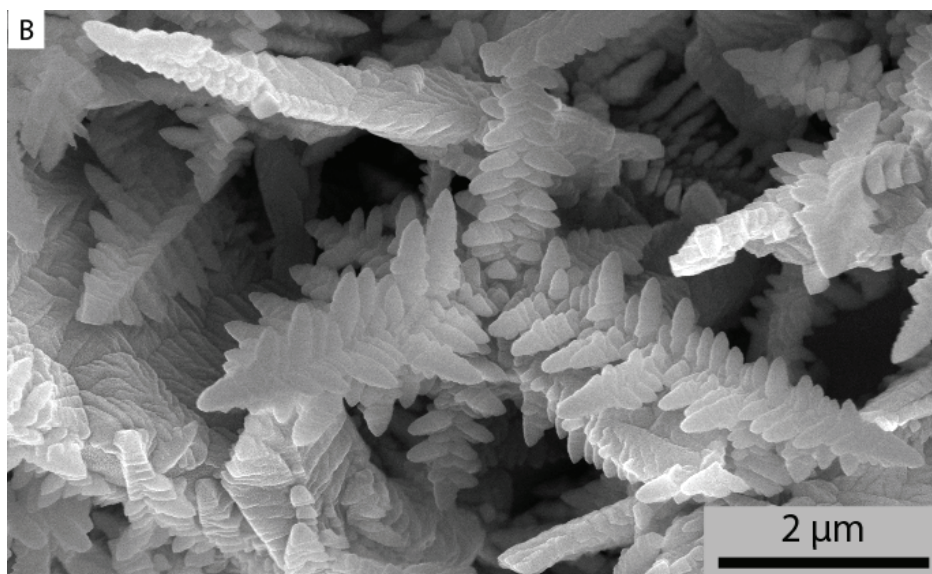
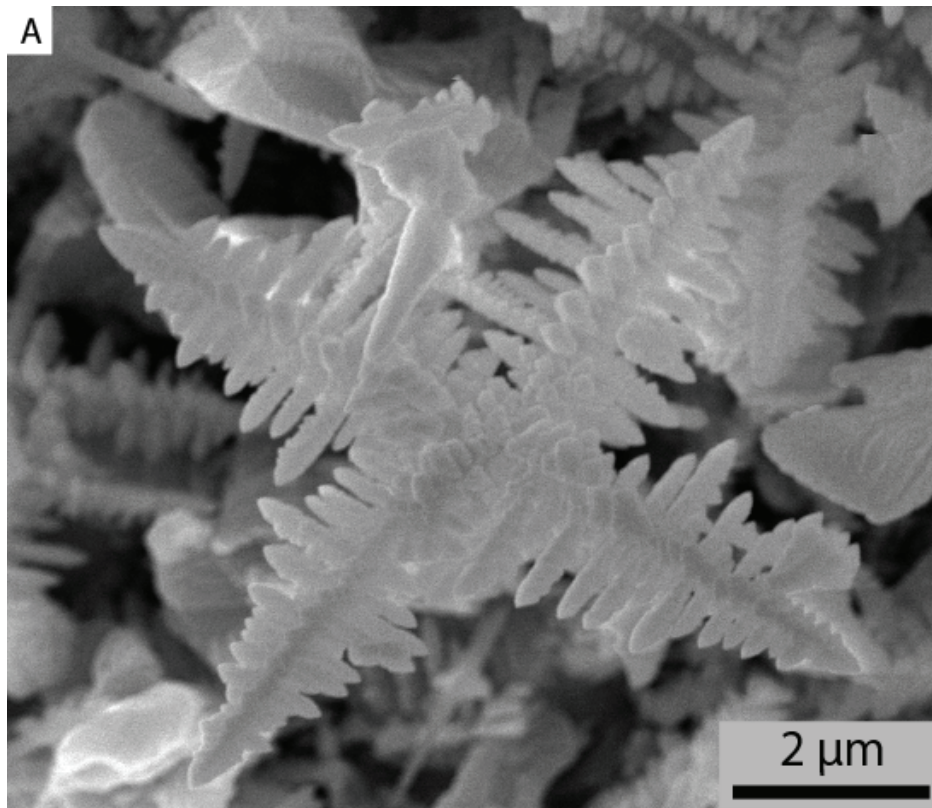


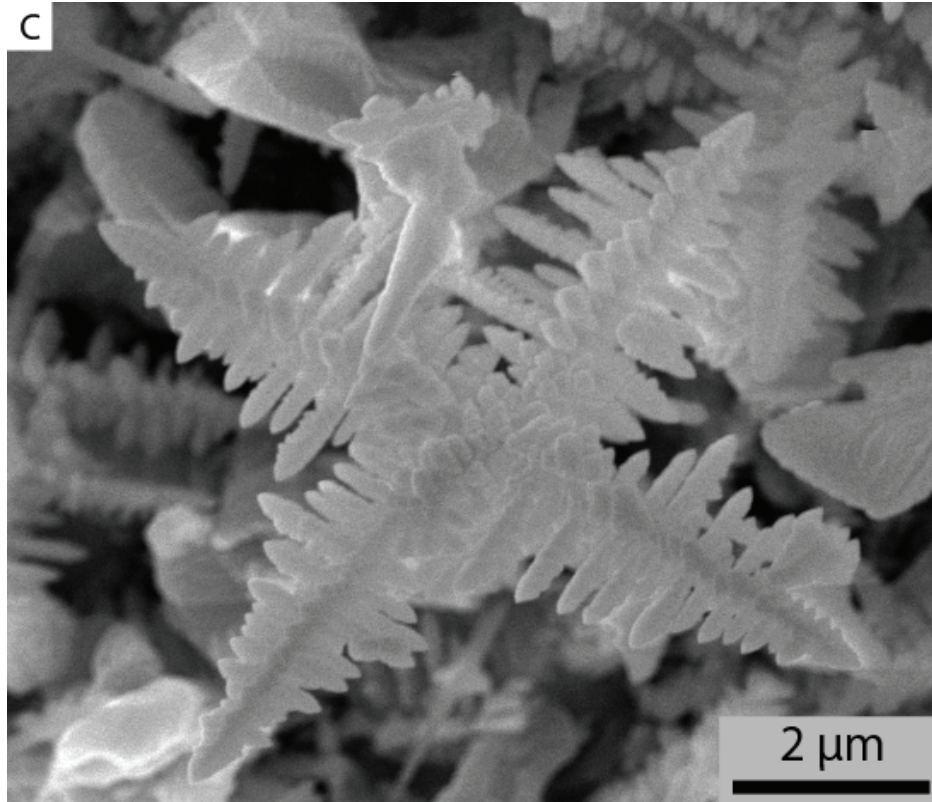
Figure 7.24: SEM images A) pre conversion and B) post conversion of nanostructure CPTi foil at 200°C for 20 hours in 0.1M Ba(OH)₂.



continued

Figure 7.25: SEM images showing the variety of structures produced by hydrothermal conversion at 200°C for 20 hours.

Figure 7.25: Continued



Not all hydrothermal conversions resulted in the production of dendrites growing vertically out from the substrate. Occasionally, dendritic structures would be observed growing in plane with the substrate as shown in **Figure 7.26**. Again, a combination of dendrites and elongated rectangles were observed as a result of the conversion process but in this sample, only a few dendrites were growing out vertically from the sample. The majority of the dendrites were growing in plane. A sample converted at 215°C for 16 hours also showed interesting morphologies as observed in **Figure 7.27**. Dendrites forming in plane with the substrate are seen throughout this sample but there was also an abundance of the rectangular morphology formations. What makes this sample

interesting is the way the rectangular formations arranged themselves. In some areas of the sample the morphologies were observed coming out from the substrate at multiple angles to one another as shown in **Figure 7.27 A**. The rectangular morphologies were observed stacked on top of another. When the edge of the sample was imaged, this stacking behavior was also observed however it took on a different arrangement as shown in **Figure 7.27 B**. Here we see many of the rectangular morphologies aligned in sets such that they form stacked wire-like formations that stick out several microns from the substrate. It is as if the rectangular morphologies attached themselves to the sides of the stacked type NWs discussed in Chapter 6.

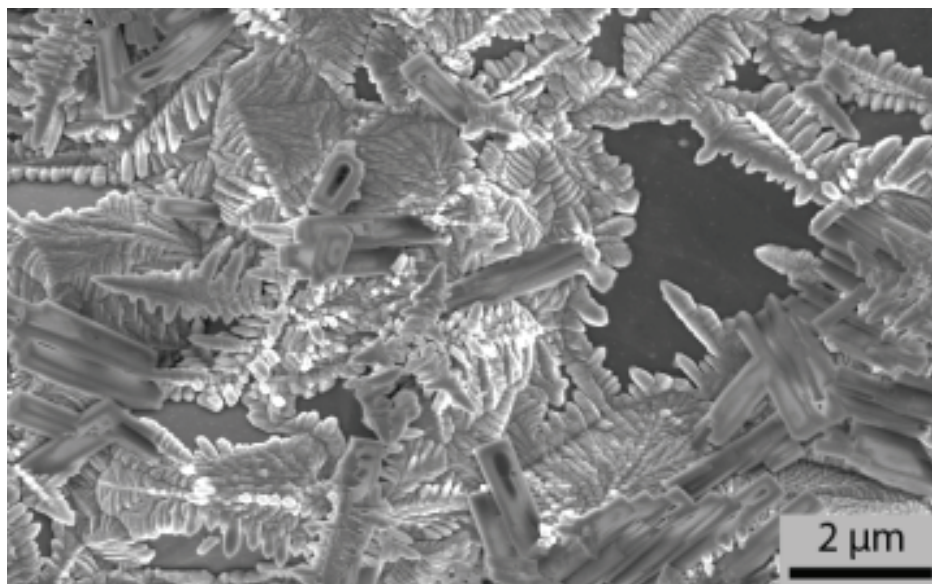


Figure 7.26: SEM image of dendrites growing in the plan of the CPTi foil substrate. Sample was converted at 200°C for 16 hours.

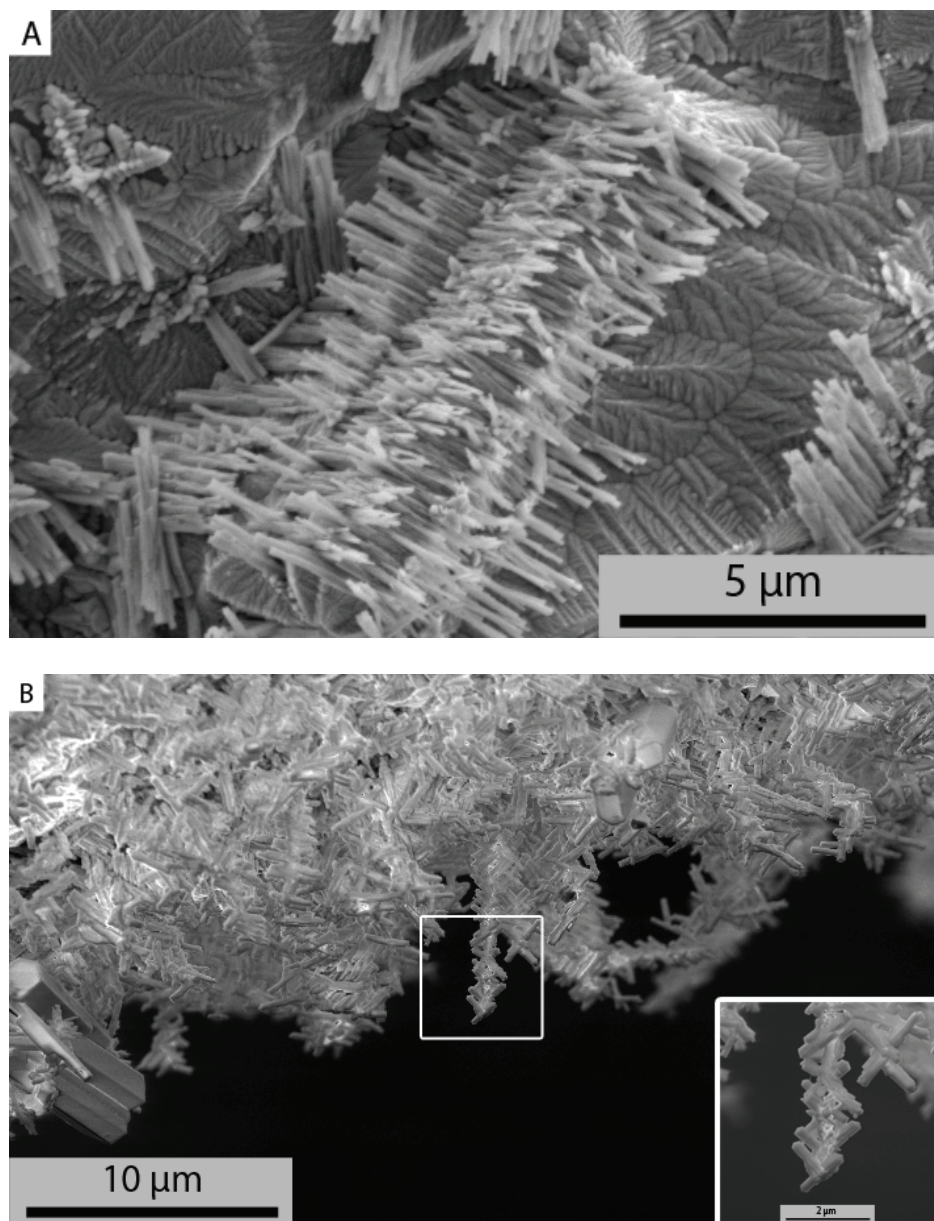


Figure 7.27: SEM images of non-dendritic structures formed by conversion at 210°C for 16 hours.

The final morphologically different structure observed resulting from the hydrothermal conversion of nanostructured TiO₂ substrates is shown in **Figure 7.28**. Rod and star like structures were observed after conversion at 200°C for 16 hours using a Ba(OH)₂-H₂O

precursor. The rods were up to 20 μm in length and one or more microns in diameter. The star shaped morphology appeared to be a small clustering of the rods growing out from one another. Rod-like structures were observed forming during the oxidation of the CPTi foil precursors in wet argon. Thus, there was some discussion that the rods observed in **Figure 7.28 A** were left over unconverted TiO_2 from the nanostructured substrate. To investigate this possibility, images of the rods were taken using the electron backscatter detector on the SEM. Backscattered electrons are scattered more strongly by heavier elements than lighter elements. This variation in the backscattered electron intensity provides contrast based on the composition of the sample being imaged. Structures made up of heavier elements such as Ba will have higher brightness in the resulting image than those made up of lighter elements such as Ti. **Figure 7.29 B** shows the corresponding backscattered electron (BSE) image for the standard secondary electron (SE) image in **Figure 7.28 A**. If the rod like shapes were unreacted TiO_2 remaining from the original nanostructured precursor, they should show a significant contrast difference to the in-plane dendrite growth surrounding the rods when imaged via BSE. This however is not the case. The rods, in-plane dendrite growth and star type structures all show similar contrast in the BSE image (**Fig. 7.28 B**). There are what appear to be holes or gaps in the in-plane dendrite growth that appear darker in the BSE image. These may be small unreacted areas where the TiO_2 substrate is exposed.

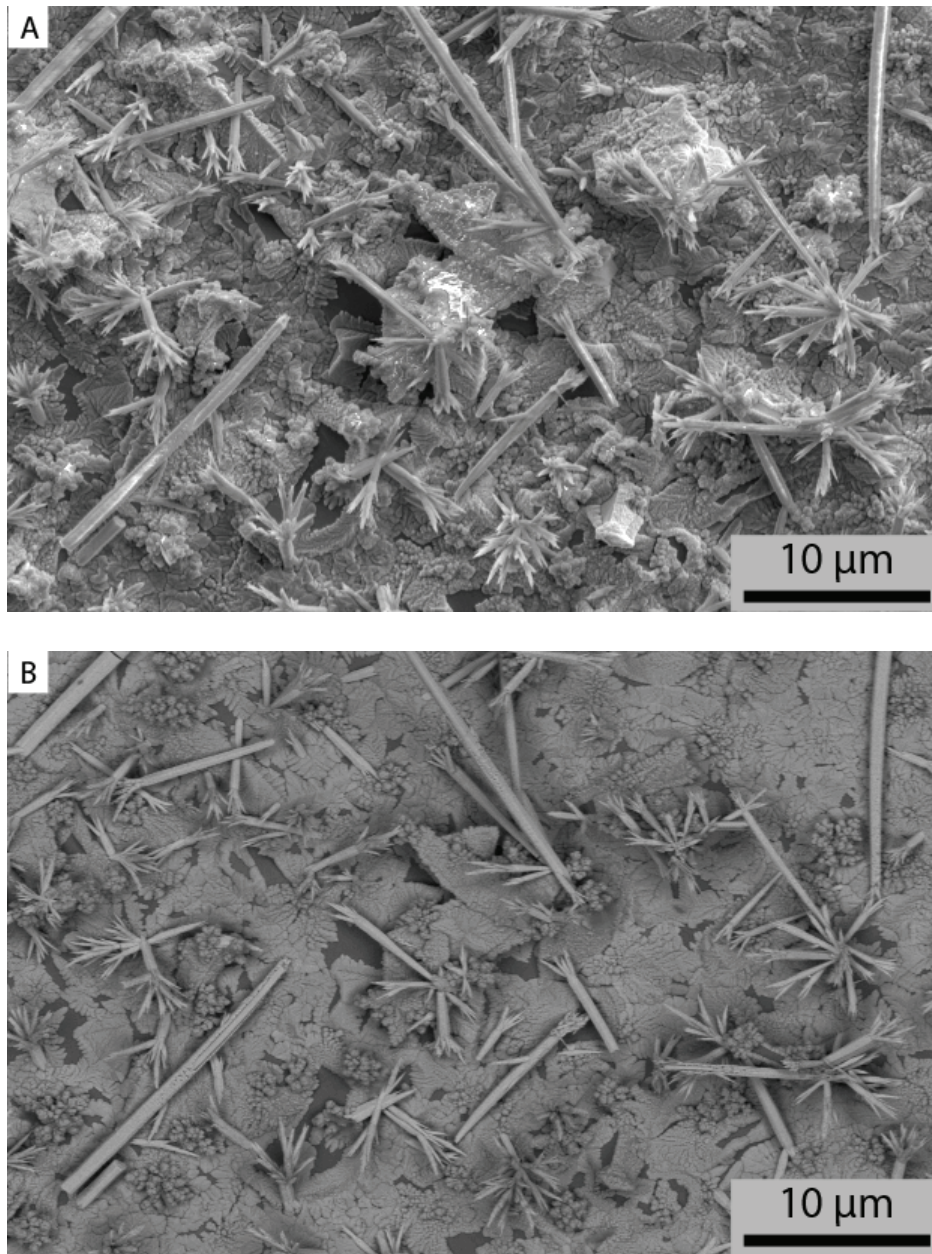


Figure 7.28: SEM micrographs showing A) secondary electron (SE) and B) backscattered electron (BSE) images of rod and star like morphologies observed resulting from conversion at 200°C for 16 hours.

The hydrothermal process used to produce the previously presented morphologies is not yet well understood or optimized. The impact of the morphology of the nanostructured

TiO₂ substrate, conversion temperature, conversion duration, and barium precursor have on the resulting titanate composition and morphology also require further characterization. Future studies are required to identify the role each of these elements plays in the dendrite formation.

7.3.4.4 *Ferroelectric Testing*

Though the process is not fully understood the resulting structures have been shown by XRD analysis to be at least partially BaTiO₃. BaTiO₃ in the tetragonal phase is a ferroelectric material. Ferroelectrics are a class of materials which display spontaneous electrical polarization when an external electric field is applied.[211] This polarization can be switched by reversing the polarity of the applied electric field. Barium titanate has been of interest as a ferroelectric material for some time since it exhibits ferroelectric behavior at room temperature.[212] Two polarization states exist within a ferroelectric material in the absence of an applied electric field. When the material is subjected to an applied field, the polarization states within the material align with the direction of the applied field. This behavior results in a hysteresis loop in the polarization vs. applied field plot. This is an important property of ferroelectric materials which contains a wealth of information including the net polarization known as the spontaneous polarization, the polarization at which all domains are oriented in the same direction or the saturation polarization, the remaining polarization after the applied field is removed or remnant polarization, and the coercive electric field strength that is the applied electric field strength needed to return the polarization to zero. An example of an ideal ferroelectric hysteresis loop is shown schematically in **Figure 7.29 A**.

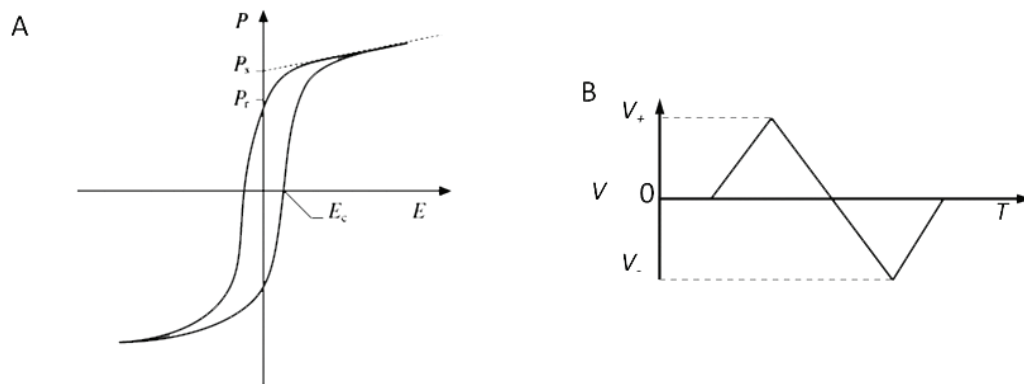


Figure 7.29: A) An ideal hysteresis loop for a ferroelectric material with its B) corresponding applied waveform.[213]

A large number of dendritic BaTiO₃ samples were subjected to hysteresis loop measurements using frequencies of 500 Hz and 1 kHz and voltages between 0.5 V and 10 V to investigate their ferroelectric response. For the hysteresis loop measurement a voltage waveform is applied such that the voltage is swept from 0 V, to a desired maximum positive voltage, down to a minimum voltage and back to 0 V as shown schematically in **Figure 7.29 B**. Initial testing results showed that the foils had ferroelectric characteristics but the resulting hysteresis loops did not have the ideal shape as observed in **Figure 7.30**. Maximum and minimum polarizations were achieved when the respective electric field was applied but almost no remnant polarization was observed. The lack of remnant polarization was suspected to be caused by a partially converted foil which may have contained phases other than tetragonal BaTiO₃, the only phase to exhibit ferroelectric behavior at room temperature. To investigate this, samples were annealed at

500°C and 650°C for 3 hours with goal of transforming any other barium containing phases to the room temperature tetragonal phase.

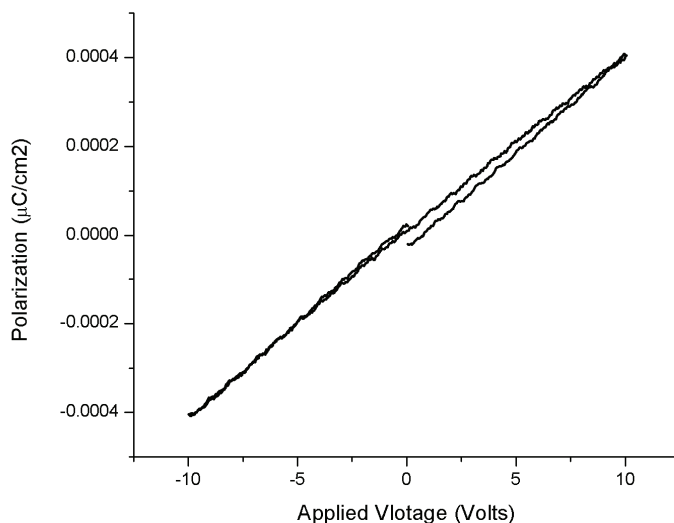


Figure 7.30: Initial results from hysteresis measurements made on converted foils.

Testing of the annealed samples revealed an increase in the remnant polarization but a decrease in the spontaneous polarization of the annealed samples. This indicates an increase in the amount of ferroelectric response of the sample. Polarization curves for the as converted, 500°C annealed, and 650°C annealed samples are shown in **Figure 7.31 A-C**. A change in both the spontaneous and remnant polarizations can be observed for each graph. An XRD spectrum obtained from the 650°C annealed sample (**Fig. 7.32**) has a lower background and sharper peaks compared to the as converted sample shown in **Figure 7.21**. The reduction in noise and sharpening of the X-ray intensities could be

attributed to the transformation of intermediate phases of Ba-Ti-O to the tetragonal phase of BaTiO₃. This could explain the change in hysteresis measurement results observed for the annealed samples.

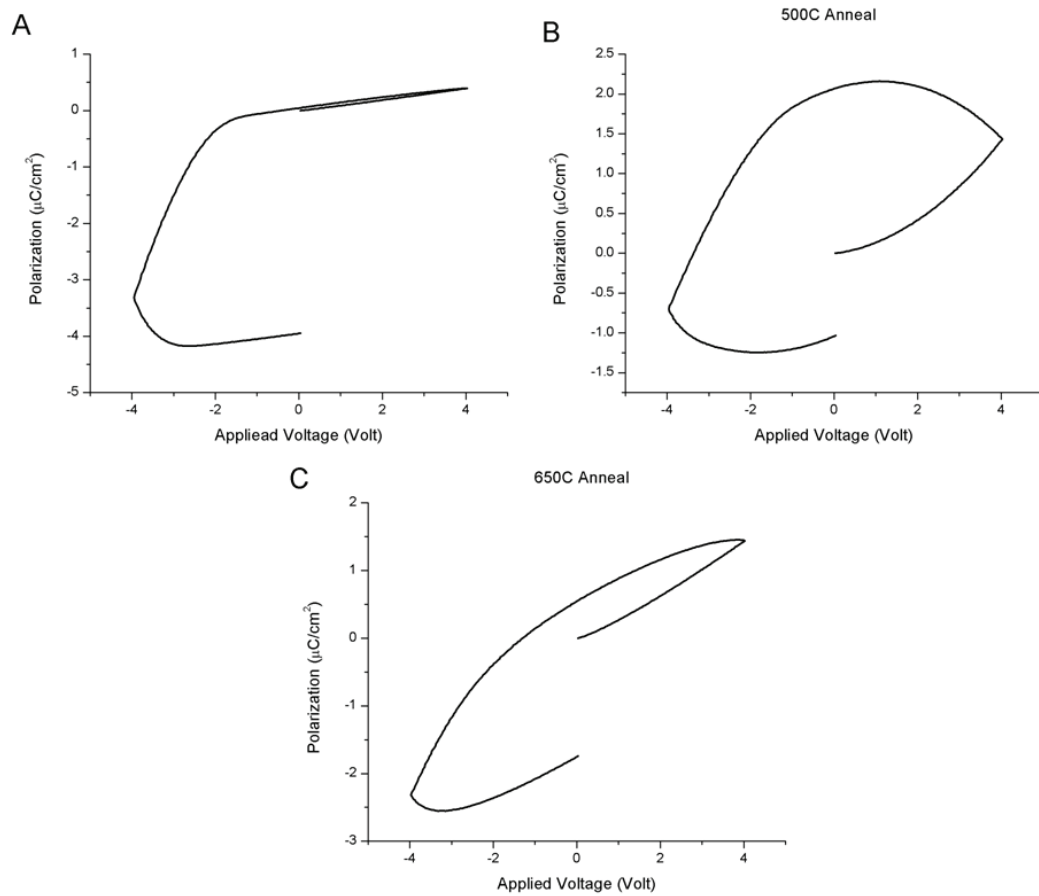


Figure 7.31: Graphs showing the change in hysteresis loop measurements as a result of annealing at B) 500°C and C) 600°C.

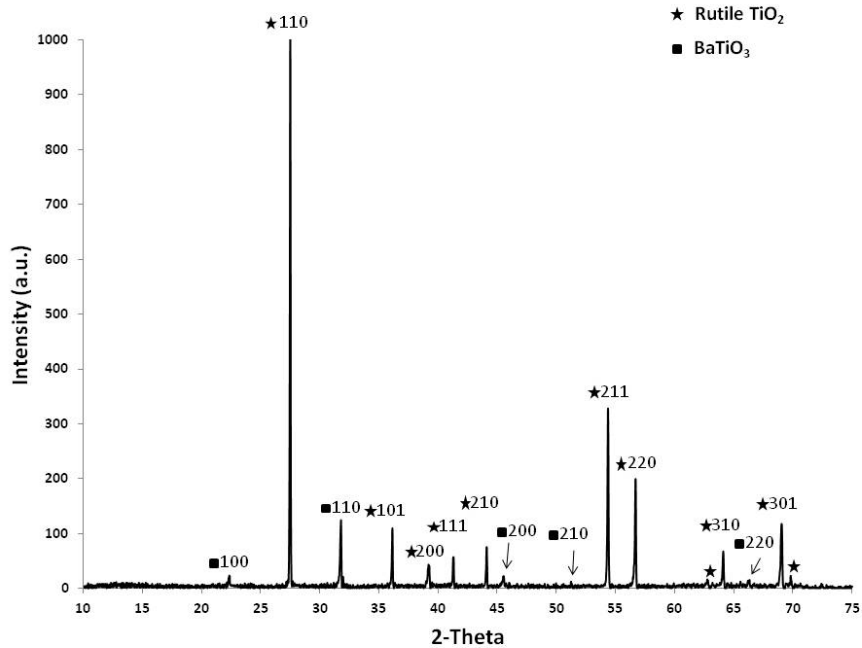


Figure 7.32: XRD spectra obtained from a converted sample annealed at 650°C for 3 hours.

The graphs shown in **Figure 7.31** are indicative of loss mechanisms at playing a role in the hysteresis measurements. Miller *et. al.* noted similar shaped hysteresis loops while conducting a study of the loss mechanisms in single and polycrystalline barium titanate.[214] They found the most common forms of loss came from the electrical contacts used in polarization measurements and from the recent history of the sample in terms of hysteresis measurements. Both of these elements may be playing a role in the poor ferroelectric response of the converted foils. The bottom electrical contact was made by attaching a Pt coated Si wafer to the bottom side of the foil using Au paste while the top electrode was deposited by e-beam lithography. The top electrode was 1 mm in diameter but only 250 nm thick. The sample roughness of the converted foils containing

dendrites was microns in scale. It was quite possible that only a very poor electrical contact was made with the sample. The polarization tests were conducted using a single loop hysteresis measurement. This may leave the sample in a polarization state that allows for losses to manifest themselves in subsequent testing of the sample. Future testing should be conducted such that the history and “memory” of the sample are accounted for. Thicker electrical contacts should also be used to help insure a strong electrical connection is formed between the sample and the measuring equipment.

7.3.4.4.1 Curie Temperature Investigation

A qualitative investigation of the effects of temperature on the hysteresis loop was conducted to test whether the Curie temperature was consistent with reported values. For this test, a sample was fitted into a 4-point probe with a heated stage capable of reaching 400°C. Measurements were taken at 25°C intervals from room temperature to 350°C to see the effect of temperature on the polarization curves. The actual sample temperature was measured using an infrared thermometer. **Figure 7.33** shows the results of this experiment. No significant change in the hysteresis loops is noted until the sample temperature was above 140°C. Once above this temperature no remnant polarization was observed. This indicates that the Curie temperature is between 100°C and 140°C which is in agreement with the reported values in the literature for barium titanate (125-136°C).^[210, 215-217] Finer temperature measurement was not possible given the experimental limitations at the time.

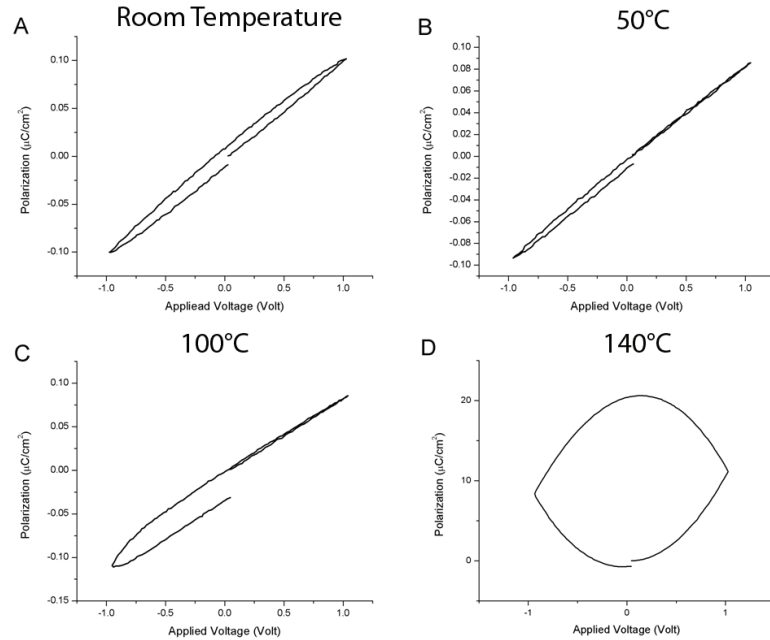


Figure 7.33: Hysteresis loop measurements taken at A) room temperature, B) 50°C, C) 100°C and D) 140°C to qualitatively look for a change in ferroelectric behavior above the Curie temperature.

Dendritic barium titanate was formed by hydrothermal conversion of nanostructured TiO_2 substrates. A variety of barium containing structures has been observed as a result of this process. XRD analysis indicates the conversion product is at least in part BaTiO_3 . The effects of conversion temperature and duration require further investigation to gain a full understanding of their influence on the resulting titanate morphology. Early polarization studies show that the resulting films exhibit some ferroelectric behavior. This behavior improves with annealing of the converted sample in air. Further studies should be conducted to investigate the effects of annealing not just on the ferroelectric response, but also on the structure of the dendrites as well. The Curie temperature was found

qualitatively to be between 100°C and 140°C which is consistent with relevant literature. Future studies should involve the characterization of individual dendrite properties.

7.4 Conclusions

Several applications for NWs produced by oxidation of Ti and Ti alloys have been investigated as a means of expanding the utility of these easy, on-step methods of producing TiO₂ NWs. NWs produced on Ti alloy substrates show significant promise as coatings for biomedical implants to increase cell adhesion and proliferation. However, this work is in the earliest of stages and further trials are required to establish the effectiveness of this coating method towards increasing cell adhesion and proliferation on actual human bone cells. To date, studies have only been conducted using HOS cells which behave similar to bone cells but are not actually part of the bone system. Though this work is exciting more research is required before the coating processes can be fully exploited.

Nanostructured Ti₅₋₅₋₅ particles were shown to exhibit a response when exposed to a reducing gas however several challenges must be overcome before they can be utilized as a commercial platform for chemical sensing. A drifting background resistance was observed for the nanostructured particles in the testing environment. This is most likely due to continued oxidation of the samples but must be remedied before the particles can be useful for sensing applications. Currently this work is ongoing with our collaborators in Malaysia who are investigating the use of oxidized Ti₆₄ particles as the chemical sensing platform. Recently they have reproduced the nanostructured growth on these particles and are investigating ways to reduce the particle size. This should allow for a

more uniform sensing film and decrease the amount of source material available for oxidation in the testing environment. Additional optimization of the NW growth process to decrease the likelihood of later oxidation of the sample is also required.

Recently, an investigation into the use of the NWs as ultra short and intense x-ray sources has begun. This first required the scale-up of the NW growth process by oxidation of Ti alloys which proved to be non-trivial. It required a careful investigation of the oxygen consumption during the growth process and its dependence on the surface area of the Ti alloy sample. With this information it was possible to predict the minimum amount of oxygen to be supplied throughout the growth process. Only once NW production was scaled-up to larger substrates could the x-ray emission investigation begin. This is the current state of this research. Large NW covered Ti64 targets are being produced and preliminary x-ray emission data is being collected.

Dendritic barium titanate produced by the hydrothermal conversion of TiO_2 NWs is of particular interest due to the ferroelectric properties of BaTiO_3 and the range of size scales afforded by the dendritic structure. A variety of morphologies have been observed resulting from the conversion of the TiO_2 NWs, however the factors that influence these morphological differences are not yet well understood. This research has been taken on by a new group member who is tasked with further characterization and optimization of the hydrothermal process and the resulting morphologies.

The NWs produced by the oxidation of Ti and Ti alloys have been shown to be applicable in a wide range of applications and industries. Research is ongoing to take these simple

processes for producing titania nanostructures and apply them to current industry needs and challenges. While obstacles exist for full implementation of the processes in several of the previously discussed applications all show promise.

Chapter 8: Conclusions and Future Work

The preceding chapters have presented two methods for producing NWs on titanium substrates. The first produced NWs on titanium alloys, particularly those containing aluminum, by oxidation in a controlled oxygen environment. The second improved the length and yield of NWs on commercially pure titanium samples by oxidation in wet argon. The following sections discuss some of the conclusions drawn from the production of NWs by each of these methods as well as suggest directions for future studies.

8.1 Growth in an Oxygen Deficient Environment

Oxidation of titanium alloys containing aluminum in an oxygen deficient environment has been shown to produce titania nanowires (NWs). The wires are core-shell in structure consisting of a rutile TiO_2 core and an alumina (Al_2O_3) shell. The optimum growth conditions that produced NWs on the Ti alloy samples can be summarized as follows: a high initial oxygen concentration at the start of the furnace ramp (e.g. 20% O_2) followed by a very low oxygen concentration (e.g. 17 ppm) for the remainder of the anneal, an annealing temperature of 700°C , an Ar flow rate of 500 sccm, for a total oxidation duration of approximately 8 hours. Using these conditions NWs were successfully grown on a number of Ti alloys. This process was successfully transferred to a variety of substrate configurations including bulk, powders, foils, and thin film.

The temperature and oxygen concentration were found to have the greatest impact on the morphology of the resulting oxide. It is important to note that the full range of temperatures and oxygen concentrations which are capable of producing NWs on alloy substrates have not been completely characterized. A more thorough investigation of the relationship between oxygen concentration, temperature, and NW production is warranted. However, some general conclusions can be made:

Experimental results indicate NW growth on titanium alloys requires a deficiency in oxygen for the NWs to form. The deficient oxygen environment ensures that only the most chemically active sites on the surface of the metal oxidize. In situations where an abundance of oxygen is present, all sites for oxidation are active as there is no competition for the oxygen atoms. However, when there is a lack of oxygen only the strongest oxygen binding locations receive oxygen atoms.

The initial oxygen concentration in the reaction chamber during oxidation is of critical importance. A significant drop in the oxygen concentration has been observed during early oxidation times. This reduction in concentration has been attributed to fast initial oxidation of the alloy samples developing an oxidation layer which limits further oxidation to only the most active oxidation sites.

8.1.1 Impact of Aluminum

The oxygen deficient growth process works on commercially pure titanium though the NW yield is quite low compared to the alloys containing aluminum. This indicates that aluminum is not absolutely required for NW growth but when present, plays a significant

role in NW formation. Some of the results and conclusions drawn from experimental work for the role of aluminum in NW formation can be summarized as follows:

The shell layer of the core-shell NWs appears to be corundum (Al_2O_3). *It is suggested that the corundum layer which forms on the outside of the rutile core prevents lateral growth of the NWs thus confining the growth to 1-D.*

Aluminum segregation to the surface of the oxide layer during oxidation has also been observed and has been attributed to the formation of an alumina surface layer. This surface layer acts as an oxidation inhibitor to the underlying metal. The migration of titanium atoms to the surface of the oxide is then limited to defects in the alumina surface layer, most likely grain boundaries. This results in titanium oxidizing at only discrete locations on the surface of the sample.

Thus it can be concluded that the role of aluminum in the production of NWs is two-fold. The first is to inhibit the formation of titanium oxide to few locations to form titanium oxide nuclei. Second, once the nuclei have formed it restricts the lateral growth of the nuclei by forming alumina on its sides thus limiting further growth in those directions. It is not clear why the alumina clad layer does not over take the nuclei or NW and encapsulate it in an alumina coating. Further studies are required to investigate this.

8.1.2 Impact of the β Phase of Titanium

One additional anomaly in the growth of NWs on alloy substrates versus the pure titanium substrates is the observed preference for growth on the β phase of titanium. This, like the impact of aluminum, has not been fully explained though some discussion and hypotheses can be made. First, it is important to realize that multiple elements of the

oxidation process both on α and β titanium could be impacting the preferential growth on the β phase. Additionally, the diffusivities of these elements are not the same in both phases. Second, the oxygen solubility in β titanium is significantly less than in α titanium. Both of these properties of the β phase of titanium can be playing a role in the observed increase in NW production.

The diffusivities of aluminum, titanium, and oxygen have all been reported to be higher in the β phase of titanium. This could lead to an increase in the reaction kinetics for the oxide formation on the β phase compared to the α . This increase could result in the early formation of the oxide structure which promotes 1-D NW growth. Since the growth on the β phase would occur earlier in the oxidation process the NWs on β would have access to the growth environment for a longer time than those formed on α thus explaining the increased NW production on the β phase.

Due to the low solubility of oxygen in the β phase of titanium only a small amount of oxygen is required to form an initial oxide layer compared to the α phase. This too would result in the early formation of the oxide layer required for NW growth and as such, the growth would occur for a longer time on β resulting in increased growth as compared to α .

Thus, the improved NW growth on the β phase of titanium can be attributed to the earlier formation of the oxide layer which promotes the highly anisotropic growth of the NWs.

8.2 Nanowire Growth on Commercially Pure Titanium

The growth of NWs on CPTi has been observed in both dry argon and wet argon. The NWs produced in dry argon were extremely short and their coverage on the sample was

extremely low compared to NWs grown on alloy samples in the same environment. The poor NW growth has been attributed to the lack of both aluminum and the β phase of titanium as these have been shown to provide direct improvement to the growth of NWs in $\alpha + \beta$ and β stabilized alloys. *However, it can be concluded that neither aluminum nor the β phase of titanium are absolutely required to produce NWs on titanium alloys in an oxygen deficient environment.*

To improve the yield of NWs on CPTi substrates, a heat treatment evolving wet argon can be employed. The following discussion outlines some of the conclusions which can be drawn from experiments conducted in the wet argon environment.

8.2.1 Growth in Wet Argon

The oxidation of CPTi in wet argon has produced numerous oxide structures. Most of these structures occur at multiple size scales and under several different oxidation conditions. The nanostructures observed include stacked NWs, nanoribbons, rods, and plateaus. *The oxidation parameters were found to have little effect on the shape of the resulting structure.*

Multiple tip formations have also been observed but these appear to simply be variations of similar morphologies. That is small rounded tips aligned with the wire's axis, flat tips with slightly larger diameters than the trunk of the wires that end abruptly, faceted heads that bend back towards the wire trunk ending in a point, and highly faceted tips that come to a sharp point have all been observed but at different size scales. *Based on the shape of the tip it is likely that the specific morphology for a given tip is a result of the cooling*

rate of the oxidation process. However, further studies are needed to confirm this conclusion.

8.2.1.1 Impact of Growth Conditions

Oxidation of CPTi samples in wet argon has produced some extraordinary NW morphologies as was discussed extensively in Chapter 6. The morphology of the NWs was virtually independent of oxidation parameters as long as NW production was obtained. That is, all nanostructure morphologies observed resulting from this oxidation process were observed over a wide range of oxidation conditions though their relative size scales changed. The average size, specifically diameter, of the nanostructures was found to increase with increasing temperature. The length of the nanostructures also increased with increasing temperature though the increase was not as profound. What was specifically interesting was while a change in the average size of the nanostructures increased with increasing temperatures their morphologies did not significantly change. Stacked wires formed at lower temperatures were morphologically similar to stacked wires grown at higher temperatures resulting in much larger size scales. *This indicates the shape of the nanostructures is a result of the oxidation process of titanium in wet argon and not the specific oxidation parameters used.*

An increase in the flow rate of the wet argon resulted in an increase in the density of nanostructure coverage on the CPTi samples. The flow rate of the wet argon was found to have a direct impact on the relative humidity (RH) in the reaction chamber. It is most likely the change in RH that impacted the nanostructure formation rather than simply the flow rate. A reduction in RH would indicate a reduction in the oxygen concentration in

the chamber. *Much like the growth in dry argon for the alloy wires, a lower oxygen concentration resulted in an increase in the coverage of nanostructures on the titanium samples.*

Temperature was found to play an important role in nanostructure formation under wet argon. At low temperatures (600°C) and flow rates (high RH) no nanostructured growth was observed. However, even at 600°C nanostructured growth could be induced by increasing the flow rate of the wet argon. *This points to a strong relationship between the oxygen concentration and oxidizing temperature for nanostructured growth similar to that observed in the dry argon experiments on the alloys.*

Nanostructured oxides were observed resulting from a wide combination of growth parameters however some trends were identified. As the oxidation temperature increased, the average size of the oxide structures increased. Also, as the flow rate of the wet argon increased, an increase in the density of the resulting structures was observed. At long oxidation times 3-D networks of nanostructures were observed.

8.2.1.2 Crystal Structure of Nanowires

All nanostructures grown on CPTi substrates that were investigated by TEM were identified as single crystal rutile TiO_2 . This is not terribly surprising given the stability of rutile in the titanium oxygen system but what is surprising is that all of the nanostructures, formed in the wet argon process, which were examined by TEM proved to be single crystals. What makes this so surprising is the drastic turns and bends the structures make as illustrated in **Figure 7.22**. These are extreme turns for a single crystal to make without any evidence of a grain boundary. Upon first examination the shape of the

NW in **Figure 7.22** would indicate double cross-slip had occurred. This cannot be ruled out but to-date, no defect in the NW has been observed which would confirm this.

The NW growth axis for both the stacked and ribbon structures was shown to be parallel to the $\langle 101 \rangle$ family of \mathbf{g} vectors. This indicates that both of these NWs, though significantly different in morphology, grow along the same crystallographic direction. Further characterization is required to pin down the growth direction conclusively. Once this analysis is completed for each of the morphologies, we can confirm whether or not the growth directions are the same.

8.3 Future Work

Much is still unknown about both methods for the production of nanostructures on titanium and titanium alloys presented in this document. As such, both processes and their resulting nanostructures are ripe for further study. The final sections of this chapter are focused on outlining some possible avenues for further studies of these processes and structures. Much of what is presented in the following sections has been mentioned at various points in this document but is assembled here for ease of locating and referencing. Future studies for both processes are presented in their respective sections.

8.3.1 Further Studies in the Ti Alloy System

8.3.1.1 Characterization of Core-Shell Structure

Extensive investigations into the structure and formation mechanism for the growth of NWs on titanium alloys under a limited supply of oxygen have been conducted however several areas are still unexplored or require further investigation. One such area deals with the characterization of the shell layer in the core-shell NWs. Recent studies have

indicated the presence of both corundum (Al_2O_3) and rutile TiO_2 in the wires. Diffraction contrast in conventional BF TEM imaging has indicated the core is TiO_2 . Additional analysis by EDS has shown the outer regions of the wire to have a higher concentration of aluminum and the core to have a higher concentration of titanium. These results would indicate the core is indeed rutile TiO_2 and the shell is corundum. However, further studies employing DF imaging using diffraction spots from the rutile and corundum diffraction patterns are needed to verify the structure of both components. The goal would be to have a known low-index \mathbf{g} vector from a corundum pattern selected to form a DF image showing diffraction is only from the shell layer. Likewise, using a \mathbf{g} vector from a rutile diffraction pattern to form a DF image where the core is bright would show that the core is indeed rutile. In several TEM images of the core-shell NWs the outer shell layer appears to be made up of many small grains. Analysis via TEM is required to fully characterize not only the shell's crystal structure, but also its morphology. The DF imaging of the shell layer should also confirm whether the shell is single crystal or made up of several individual grains.

8.3.1.2 Characterization of Oxide Formation

Quenching experiments have been conducted at short time intervals to interrogate the formation of the oxide layer formed on the alloy samples during oxidation. This was done by air quenching the samples at various stages in the oxidation process and creating cross-sectional foils for investigation by TEM and EDS. Initial results showed a segregation of aluminum and titanium after only a short time of oxidation however crystallographic data has not yet been collected. That is, compositional profiles through

the oxide layer and base metal have been collected for three oxidation durations but not diffraction data. Thus, we know the compositional make-up of the oxide layer and the metal directly underneath but we do not know the crystal structure and thus the phase identification of the oxide layers. XRD analysis has provided some information but it is a bulk sampling technique and cannot be used to completely explain the compositional profiles observed in the TEM. As such, HRTEM should be employed to investigate the crystal structure of the oxide layers at all three of the oxidation durations previously examined and possibly additional oxidation durations as well. This would give a better understanding of the progression of the oxidation process.

The cross sectional analysis was only performed on quenched titanium alloy oxidation samples at oxidation times of 20 min, 45 min, and 390 min. Even at the shortest time interval of 20 min the transition from the cracked oxide layer to the formation of nanoislands, stage I to stage II, had already occurred. As such, shorter time oxidation experiments should be conducted to better characterize this transition.

Additionally, the transition from nanoislands to NW growth, stage II to stage III, occurred at some point between the 20 min and 45 min quenched samples. Further analysis is required of the oxidation behavior, specifically of the surface oxide layer, at oxidation times in this interval.

8.3.1.3 Characterization of Nanowire Tip

Investigations by SEM and TEM have shown no evidence a metallic cap at the tip of NWs grown on alloy samples and as such, the VLS mechanism for NW growth has been dismissed as the formation mechanism for this process. However, there are many alloying

elements present in the system which have been used as catalyst for NW growth in other processes.[218-220] As such it would be prudent to conduct a further investigation of the NW tips to look for trace amounts of any alloying elements. An ideal technique for this investigation would be Atom Probe Tomography (APT). The APT technique removes atoms from a material layer by layer and collects them on a detector. Based on the energy of the atom when it collides with the detector the atom type can be identified. This, combined with time of flight information from the atom makes it possible to form atom by atom 3-D reconstructions of the NWs. An APT sample needs to be less than 70 nm in diameter making the NWs grown under a limited supply of oxygen ideally suited to this technique as-grown without the need for further thinning. Oakridge National Labs (ORNL) in Tennessee has facilities dedicated to this characterization technique and a proposal for this work has already been approved. Unfortunately, due to the high user load of the facility the analysis will not be completed until mid-summer.

8.3.1.4 Optimization of Oxygen Concentration

Oxygen concentration studies and in particular the work on large titanium alloy samples for x-ray emission have shown the importance of the oxygen concentration at early times in the oxidation process. There is experimental evidence which indicates a very high initial oxygen concentration that decreases over time promotes the best coverage and length of NWs on the alloy substrates. To date this type of processing has been achieved by starting the oxidation with the reaction chamber open and exposed to ambient levels of oxygen and closing the chamber and turning on the gas flow once the temperature has reached a given level, typically 200°C. While this is an effective means of improving NW

yield on the alloy substrates it is not very reproducible and becomes almost a guessing game when attempting to scale up the process for samples with increased area. For practical use, this process needs to be better optimized and standardized. Further studies investigating and optimizing a multi step process for the oxygen concentration in the reaction chamber should be undertaken.

A basic understanding of the growth process for NW production on titanium alloy samples has been developed. The governing growth parameters have been identified and many of them have been optimized. A mechanism theory to describe the transition of the oxide growth from planar to 1-D has been developed. Additionally, several applications for this technique are being investigated and show promise. There is still more to be learned and understood about both the process and the structure of the resulting NWs however significant progress has been made. Future researchers have a strong foundation upon which to build.

8.3.2 Further Studies for Growth by Wet Argon Oxidation

8.3.2.1 Unanswered Growth Questions

The yield and density of nanostructures grown on commercially pure titanium has been drastically improved by oxidation in wet argon as compared to oxidation treatments in an oxygen deficient environment. The nanostructures grown by this process have been shown to be rutile TiO₂. The morphology of the nanostructures is rather diverse and unique and makes a compelling subject for further study.

While the growth process for the production of TiO₂ NWs on CPTi substrates in wet argon has been successfully demonstrated, some questions remain unanswered: *What*

causes the different oxide structures to form? Why would one structure preferentially grow over another?

Additionally, several structures of different type have been observed growing in close proximity to one another. *Is the gas environment in that specific region significantly different from another? Is it some local variation in the substrate that ultimately dictates which structure will grow?*

High angle turns in the formation of the structures have also been observed. This is very interesting from a crystal growth point of view. *What would cause such a drastic change in growth direction for a crystal? What defects could be present to allow for this type of behavior?*

The node formation is also of specific interest. *Why and under what conditions do these nodes form? Do they more often form from an individual structure or from the intersection of two or more structures growing into one another?* While these structures are extremely interesting, they raise many questions which have not been answered. The following sections are meant to give some guidance on possible paths to finding answers to these questions.

8.3.2.2 Further Characterization of Oxide Formation

XRD analysis was only conducted on samples resulting from a small set of oxidation conditions (600°C, 700°C, and 800°C for 6 hours at 500 sccm of wet argon). Further XRD analysis is required to investigate the structure and phase composition of the oxide resulting from all parameters combinations shown in **Figure 6.5**. This may shed light on why one structure forms over another.

Also, short time oxidation experiments (< 2 hours) should be conducted to see if the initiation of NW growth can be identified. This would also allow for characterization of the oxide layer which forms at these short time scales to identify any defects or oxide formations or phases which may be causing the 1-D growth. Perhaps this analysis may also point to why a given nanostructured morphology is preferred over another.

8.3.2.3 Cross Sectional TEM Investigation

The second set of unanswered questions is not as easily investigated. It is exceedingly challenging to measure slight fluctuations in the local gaseous environment. A more attainable approach to identifying why two or more different nanostructure morphologies form in close proximity to one another would be to make cross sectional samples the area containing the nanostructures for characterization via TEM. This would allow for the collection of compositional profiles from the areas directly beneath the different morphologies, conclusively identify the phase and structure of each morphology, and investigate the occurrence of any defects in the oxide layer beneath the structures which may lead to the morphological variation.

8.3.2.4 High Resolution TEM Analysis of Angled (Bent) Nanostructures

High angled turns have been observed in almost all morphologies produced by the oxidation of CPTi in wet argon. To-date, no direct observation of any cause for this behavior has been made. To complicate matters, the NWs exhibiting behavior have been shown to be single crystal by DF TEM imaging. As such, it is advised that HRTEM be employed to look for dislocations or other defects in the bends which could account for this behavior.

8.3.2.5 3-D Network Formation Investigation

Oxidation at long times (> 16 hours) produced a 3-D network of interconnecting nanostructures. The point at which these structures form and why they form is not understood. A comprehensive study of what conditions promote formation of the 3-D network and ways to promote or inhibit its formation should be undertaken. Additionally, little is known about the early stages of oxidation for this process. All experiments were conducted for a minimum of 4 hours. Shorter oxidation durations (< 2 hours) should be explored to elicit information about the early formation of the NWs. It may also be useful to observe the influence of oxidation duration on different temperature and flow rate combinations as shown in **Figure 6.5**. Information gained from such a study could allow for further tailoring of as-grown nanostructure morphologies to suit a given application. The morphologies of nanostructures formed by this process were varied. No direct connection between processing parameters and nanostructure morphologies were made. Perhaps the most interesting morphological behavior was the bending and turning observed for several of the nanostructures. What exactly the cause of this change in growth direction is unknown, but is worthy of further investigation.

8.3.2.6 Effects of Relative Humidity on Resulting Morphology

The oxidation parameters have been explored but not as extensively as those for the alloy oxidation. For example, the RH has been measured at three different flow rates of wet argon but an exhaustive study of the effect of RH on the resulting NW growth and morphology has not been completed. Additionally, the lowest RH used in the oxidation experiments was ~85%. This is an extremely high RH. Exploration of NW growth at

lower levels of humidity would be desirable. Thus, more detailed study of the impact of RH is warranted.

8.3.2.7 Conclusive Identification of Nanowire Growth Direction

Preliminary TEM investigations of two of the nanostructures, stacked and ribbon have been conducted. These results showed both morphologies to be rutile TiO₂. A possible growth direction was identified for the wires however these results are not conclusive. Additional analysis via electron diffraction is required to pin-down the growth direction. Finally, the growth mechanism for these NWs has not been investigated. The resulting morphologies and growth rates are drastically different from the NWs produced on the alloy substrates and the oxidation environment is also significantly different. Thus, it does not seem likely that the same mechanism is at work in both processes. Therefore, an investigation into the underlying mechanism(s) which promote the growth of NWs in wet argon should be explored. This would include short time experiments to observe early NW formation, cross-sectional analysis of the samples to observe oxide growth and look for defects such as dislocations that could promote the anisotropic growth observed, and chemical analysis to investigate the roles oxygen concentration, hydrogen, and water vapor play in the formation of the NWs. There is some evidence that cooling could have some impact on the tip morphology of the NWs. The impact of cooling rate should also be investigated.

8.3.2.8 In-situ TEM Characterization

The wires grown in wet argon are excellently suited to in-situ characterization via TEM due to their short growth time and ability to be grown directly on a TEM grid. This type

of analysis would allow for direct observation of NW initiation and growth at extremely small scales. This may enable one to observe why one morphology forms over another and may give insight into the underlying growth mechanism(s).

A process has been developed which improves the NW yield on CPTi samples by oxidation. It involves the use of wet argon to promote the formation of unique nanostructures. This work is in its early stages and is well suited for future exploration.

8.3.3 Dendritic Barium Titanate

Through the use of hydrothermal techniques, nanostructures CPTi substrates have been converted to barium titanate. This process results in the formation of several morphologies of the titanate including elongated rectangles and dendrites. The dendritic morphology of barium titanate has not been reported in the literature as of the writing of this manuscript. As such, these novel structures and the process used to create them should be well understood.

8.3.3.1 Impact of Conversion Parameters

While a cursory investigation of the impact of the conversion temperature and duration on the resulting titanate morphology has been conducted, an exhaustive characterization has not. Further studies are required to conclusively identify the optimum conversion parameters which produce the dendritic barium titanate morphology. Additionally, the impact of the barium precursor used has not been investigated. Preliminary results showed that both $\text{Ba(OH)}_2\text{-H}_2\text{O}$ and $\text{Ba(OH)}_2\text{-}8\text{H}_2\text{O}$ successfully produced titanate dendrites though and extensive study to investigate if the precursor plays a significant role in the resulting morphology has yet to be conducted. The hydrothermal process used

to produce the previously presented morphologies is not yet well understood or optimized.

The impact the morphology of the nanostructured TiO₂ substrate has on the resulting titanate composition and morphology also requires further characterization. For the preliminary studies, nanostructured CPTi foils were always oxidized at 700C in 500 sccm flow wet argon for 4 hours. In Chapter 6 it was shown that the morphology of the CPTi substrate could be altered by changing the oxidation parameters. Future studies should involve an investigation of the role the starting nanostructured TiO₂ morphology plays on the resulting titanate.

8.3.3.2 Characterization of Titante Morphology

Only bulk characterization techniques have been used to identify the structure of the morphologies resulting from the hydrothermal conversion of the nanostructured CPTi substrates. XRD analysis has shown the presence of BaTiO₃ after conversion but it has not yet been confirmed that the dendrite or the elongated rectangular morphology are indeed barium titante. The sample will need to be characterized by an alternate technique to identify the structure of the individual morphologies.

A likely candidate technique is electron diffraction in a TEM. However, for this technique to be employed the dendrites will need to be electron transparent. This would require the use of a FIB-SEM to selectively mill away material from an individual dendrite. However, care must be taken to ensure that a representative sample is made from the selected dendrite. Once the sample is prepared a combination of SAD, BF and

DF imaging, and EDS profiling can be employed in a TEM to identify the phase and composition of the specific morphology.

An alternate technique which may be applicable to these morphologies is electron diffraction in an SEM by orientation imaging microscopy. This technique does not require the sample to be electron transparent as in diffraction in a TEM but also does not have the special resolution afforded by the TEM. However, if the dendrites and or elongated rectangles could be removed from the converted sample and placed on a non-crystalline substrate one should be able to obtain a pattern to conclusively identify the phase of the sample.

8.4 Final Summation

The growth of NWs on titanium and its alloys by thermal oxidation has been achieved in two environments: deficient oxygen and wet argon. The deficient oxygen oxidation is best suited for NW growth on titanium alloys and the wet argon oxidation works best for commercially pure titanium. Both processes are low cost, simple, and does not require specialized equipment or personnel. Exciting applications for the structures grown by these techniques are being pursued and show great promise as potential applications.

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